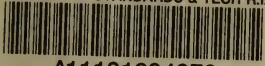


A11101 294979

NAT'L INST OF STANDARDS & TECH R.I.C.



A11101294979

/Bulletin of the Bureau of Standards
QC1 .U5 V10:1914 C.2 NBS-PUB-C 1905

THE SILVER VOLTAMETER—PART IV

THIRD SERIES OF QUANTITATIVE EXPERIMENTS AND SPECIAL INVESTIGATIONS

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I. INTRODUCTION

In the three papers ¹ preceding this the course of the work has been traced from its beginning in 1908 until the International Technical Committee met at the Bureau of Standards in April, 1910, to carry out a joint investigation of the voltameter and to determine the voltage of the Weston normal cell. The experiments that disclosed the cause of difference between the porous-pot and the filter-paper voltameters have been described. The causes for different forms of deposit and the chemical reactions taking place in the electrolytes contaminated by filter paper and similar substances have been discussed, and methods of preparing the electrolyte with tests for judging its purity have been developed. Finally, the reliability of the porous-pot form of voltameter as a standard for the measurement of electric current has been established. Our part in the work of the International Technical Committee is detailed in the report of that committee, which has been published.²

At the conclusion of the joint work some further experiments were deemed necessary, since the specifications for the voltameter had not been agreed upon and a number of outstanding questions required answers before official specifications could be prepared.

The agreement of the different types of voltameters used by the delegates had been sufficiently good, however, to enable the committee to fix the voltage of the Weston normal cell as 1.0183 volts at 20° C.

The porous-cup voltameter and a new form devised by Mr. F. E. Smith, of the National Physical Laboratory, England, had been found to be in particularly good agreement. This latter form has no septum between the anode and cathode except for a glass trap to catch the slime of the anode.

The object of the work described in this paper was, therefore, to carry out a series of experiments on these two forms of voltameters

¹ This Bulletin, 9, p. 151 (Reprint No. 194); p. 209 (Reprint No. 195); p. 493 (Reprint No. 201).

² Report of the International Technical Committee, 1912.

that should afford as complete data as possible for formulating specifications, according to which the voltameter might be used at any time for the measurement of current and (in connection with resistance standards) for checking the constancy of the Weston normal cell. This work consequently included not only a further comparison of these two forms of voltameters, but also a study of the effects of traces of uncombined acid or of base in the electrolyte, and of variations of other conditions.

II. DETERMINATION OF THE VOLTAGE OF THE WESTON NORMAL CELL

The International Technical Committee fixed the voltage of the cell to five significant figures (1.0183 at 20° C), but it is desirable to reach an accuracy sufficient to justify recording six figures. It has been our practice in the present work to give the result of each experiment as a determination of the voltage of the Weston cell rather than to assume the latter and compute the electrochemical equivalent of silver. The International Electrical Congress of 1908 defined the electrochemical equivalent of silver to be 1.11800 mg per coulomb, and we have based the calculation of the emf of the Weston cell on this value. The absolute value of the electrochemical equivalent as recently determined by the present authors in conjunction with Rosa, Dorsey, and Miller,³ at the Bureau of Standards, using the porous-cup and new form of voltameters and an absolute current balance, is very close to this figure, namely, 1.11804 mg per coulomb. The voltameter determinations on which this is based form part of the observations included in this paper, the others being made subsequently. The mean value which we give in this paper for the Weston cell at 20° C is only 8 parts in 1 000 000 higher than that recorded in the paper of Rosa, Dorsey, and Miller. It would appear from this data, therefore, that the absolute electrochemical equivalent of silver is about 1.11805, assuming that no significant change has occurred in the concrete standards for the ohm and the volt since the balance work was discontinued and assuming that the inclusions of foreign material in the deposited silver are negligible. We shall discuss the latter point somewhat further on in this paper.

³ This Bulletin, 8, p. 367 (Reprint No. 171).

A. BASIS OF REFERENCE FOR CURRENT AND VOLTAGE MEASUREMENTS

1. WESTON NORMAL CELLS

In the first paper of this series the arrangements for preserving four standard cells at a constant temperature were described. For practical work we have used one of these, cell No. 109, and by means of the other three and a large number of reference cells of the Bureau have carefully determined the relation of this cell to the mean Weston normal cell, which was defined⁴ by the International Technical Committee. Throughout the present paper the value recorded for each experiment has been reduced to this basis by adding to the number actually computed from the electrolysis experiment a correction which expresses the amount by which the voltage of cell No. 109 was lower than the mean Weston normal cell. This correction was usually about 25 millionths of a volt, but varied by a few millionths from time to time.

2. RESISTANCES

The formula for the emf of the cell is $E = \frac{MR}{1.11800t}$ where t is the time of the deposit in seconds, M the mass of silver deposited in milligrams, and R the value of a resistance standard across which the fall in potential is maintained equal to the voltage of the cell.

We have used in our recent work, as before, a resistance standard of 2 ohms, number 2342, made by Otto Wolff, and have assigned to it a value in international ohms in accordance with the definition given by the International Technical Committee.⁵

B. MEANING OF THE TERM "INTERNATIONAL VOLTS"

Our results, therefore, express the voltage of "the Weston normal cell" at 20° C in terms of *international volts*. It should be noted here that a slight ambiguity may arise as to the meaning of the term "international volts," and hence in some cases it will be necessary to state explicitly what is meant.

In accordance with the decisions of the London conference the silver voltameter is to be used to measure the international ampere,

⁴ The Weston normal cell was defined as the mean of the cells submitted by the National Physical Laboratory, The Laboratoire Central d'Électricité, the Physikalisch Technische Reichsanstalt, and the Bureau of Standards, taken by groups. In the recent paper of von Stienwehr (Zs. f. Instr., 33, p. 321) the French laboratory was not mentioned in this connection. (International Technical Committee report, p. 8.)

⁵ International Technical Committee report, p. 8.

and this in connection with the international ohm may be used to measure international volts. On the other hand, a standard cell whose voltage is expressed in terms of the mean Weston normal cell taken as 1.0183 volts at 20°C, is now the recognized method of measuring international volts in accordance with the recommendation of the International Committee on Electrical Units and Standards. The difference between the two measurements will be the same as the difference between the round value 1.0183 volts recommended by the International Committee, and adopted for use by the several countries and the more exact figure expressing precisely the value found by means of the silver voltameter and a standard resistance, assuming that the errors of measurement are negligible. From a long series of determinations with the voltameter we believe that this difference is about 3 parts in 100 000. (See p. 486 below.) However, for the present at least, the value 1.0183 should always be used in practice rather than the value given in this paper, 1.01827. In other words, the international ampere in practice should be derived from the ohm and volt (the latter being fixed by the Weston normal cell taken as 1.0183) rather than from the silver voltameter. This fact, however, does not lessen the significance of the results obtained in this paper, since one of the most important objects at present is to be able to write specifications for the voltameter and to confirm the decision of the International Committee.

C. VOLTAMETERS AND MATERIALS

In the first paper ⁶ the porous-cup voltameter and also the Pogendorff and siphon forms, which we have continued to use in the present work, have been described and illustrated. Beside these we have made use of two other forms, which we briefly describe here. The one which we have designated as the modified siphon consisted of a small glass dish 4.5 cm in diameter and 3 cm deep which was submerged in the electrolyte. From the top edge of this dish there projected upward four short glass rods that supported an annular siphon whose lower edge was just below the surface of the electrolyte. A cross section of this voltameter is shown in Fig. 1. The chief difficulty with it was that the anode

⁶ This Bulletin, 9, p. 157 (Reprint No. 194).

was necessarily small, which caused considerable anode slime, and sometimes this escaped to the cathode when the voltameter was being dismantled.

The other voltameter was Mr. Smith's new form, which possesses many advantages for work of high precision. This form has been described by him ⁷ as follows: "The voltameter has an anode in

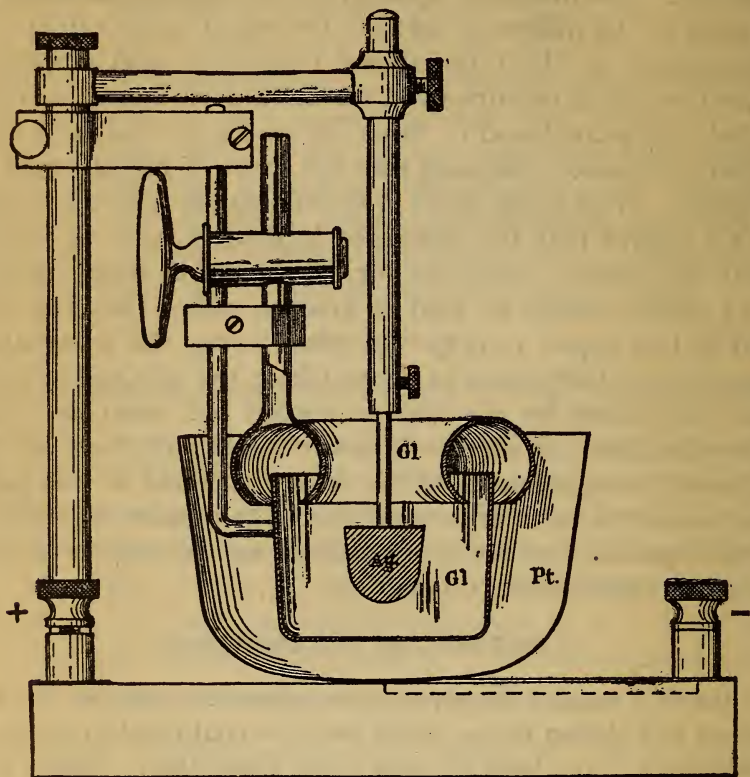


Fig. 1.—Modified syphon voltameter

the form of a silver disk coated with electrolytic silver. This disk is contained in a shallow glass basin (with ground edge) supported by a glass rod passing through the center of the disk. A glass cylinder with ground ends fits over the basin and is used to separate the electrolyte into two parts, before and after the electrolysis." Fig. 2 shows a diagram of the voltameter, and Fig. 3 a photograph of it. With the lapse of time the significance of the

⁷ The Nat. Phys. Lab. report for 1910, p. 32.

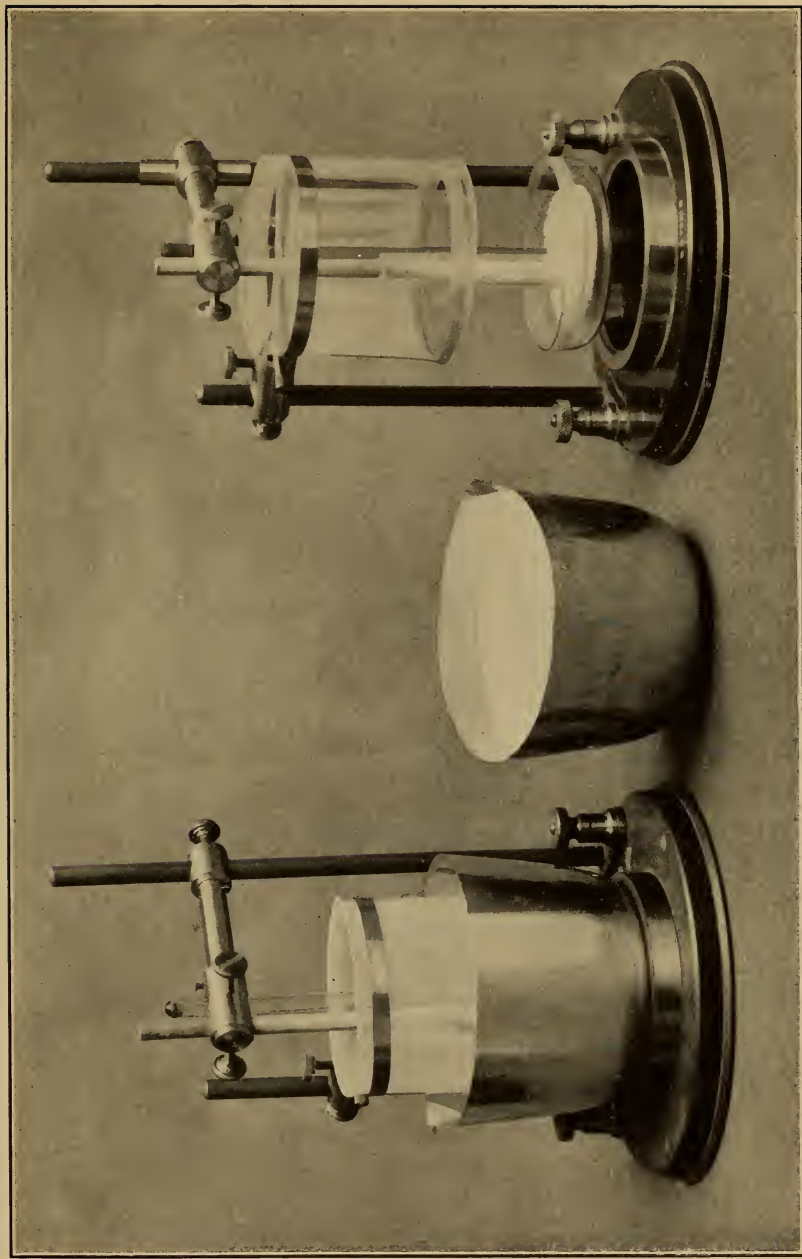


Fig. 3.—Smith form voltameter

name "new form," by which it was designated in the report of the International Committee, will vanish, and therefore we think it should be called the "Smith form" after the analogy of the Rayleigh and Richards forms.

The materials for the electrolyte used in these final experiments were of the best and satisfied the criteria that we have specified for a sufficient degree of purity. In some few cases we have employed electrolytes to which we have purposely added impurities of various kinds for the sake of experiment. We have endeavored to conduct this final series according to the best procedure learned from our previous work.

D. TABLES OF RESULTS

The experiments naturally fall into three groups, of which the first began at the close of the International Technical Committee's work and continued until September 1, 1910. The second group occupied the months of October and November, 1910, during which time the quantitative measurements were made by Mr. G. E. Post, of this Bureau, in the absence of Mr. Vinal. The last series of measurements was begun in June, 1911, and continued until March, 1912. In taking the mean values for the various forms and sizes of voltameters these three groups have been separated in Table 8, so that the results at different periods of the work may be compared.

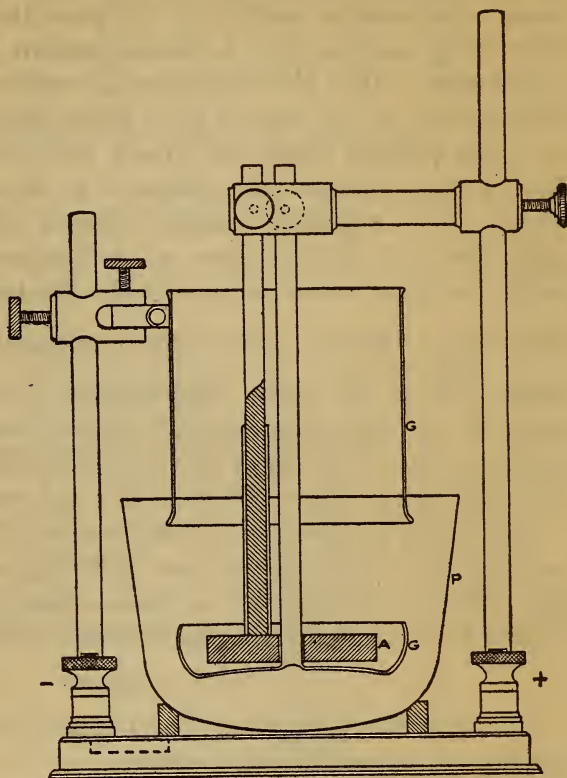


Fig. 2.—Smith form voltameter

1. CORRECTIONS FOR ACID PRESENT

We have made considerable study of the effect of small quantities of acid in the electrolyte, and our results show that when acid is present in pure electrolyte the effect is to decrease the mass of the deposit. In a number of cases we have made comparative runs, using neutral electrolyte in one voltameter, and the same electrolyte made acid to a known amount in an exactly similar voltameter. After thus obtaining a number of values to express the decrease in the deposit for a given quantity of acid present, we have plotted them and drawn the curve shown in Fig. 4. Each point represents the difference in deposit of an acid voltameter from an exactly similar neutral voltameter. Both the porous pot and Smith's form of voltameters were used in this work, and the values obtained from the latter are indicated by solid dots. The two dotted curves represent the limits of $\frac{5}{100\ 000}$ either side of the mean experimental curve. They show that most of the determinations fall within these limits so that the general shape of the mean curve is fairly well determined, at least for acidities up to about 80 parts in 1 000 000 (0.008 per cent).

Examining the curve as it stands we find that for acidities below 10 parts in 1 000 000 equivalents of HNO_3 , the correction (in parts per million) to be applied to the computed value for the cell to correct for the acid present, is sufficiently well given by the formula

$$y = -4.5 x.$$

For acidities ranging from 10 to 100 parts in 1 000 000 the following formula represents our results:

$$y = -4.5 x + 0.02 x^2$$

Beyond this point the experimental results are not sufficiently numerous or concordant to determine the form of the curve.

In Table 1 the values are given upon which this curve for the acid corrections is based. All determinations in which the electrolyte was believed to be pure are included, but the last two points are not shown on the curve. In a few instances acid tests were made on impure electrolytes and the scattering results will be discussed when the general question of acid is dealt with.

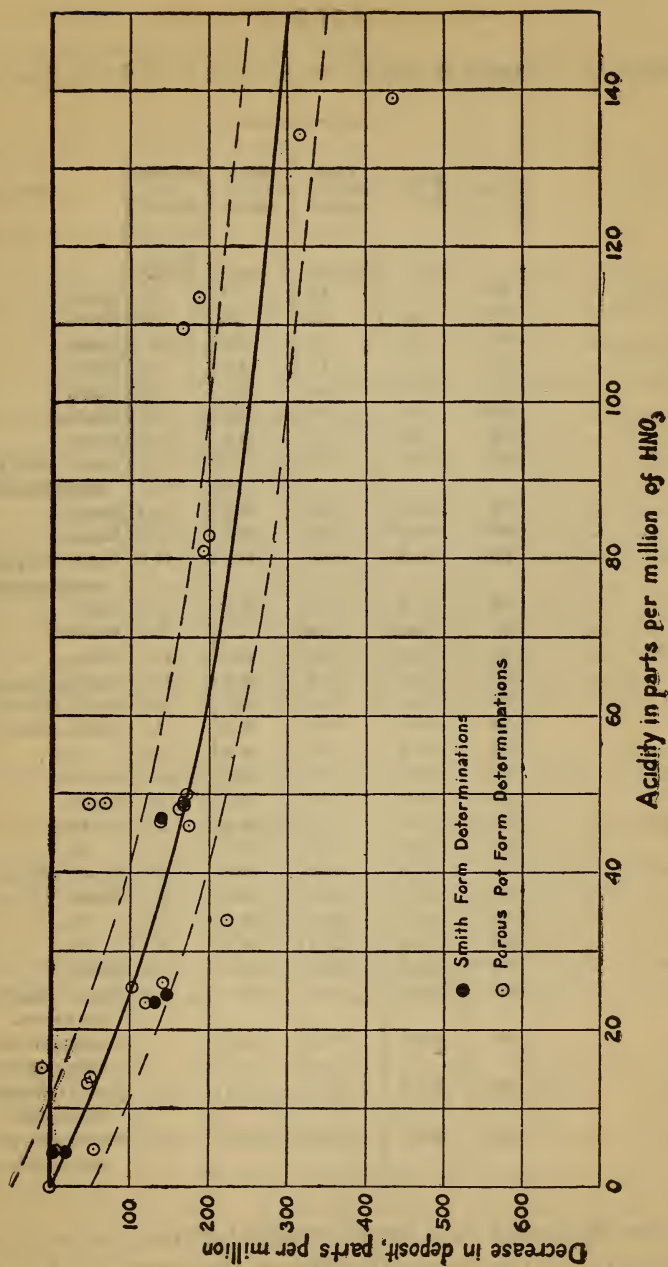


Fig. 4.—Curve showing effect of acid on deposit

TABLE 1

Relation of Decrease in Deposit to Amount of Acid in Electrolyte

[Pure electrolytes only]

Date	Form	Initial acidity	Final cathode acidity	Mean cathode acidity	Decrease in deposit	Remarks
		$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	pts. in 100 000	
Feb. 20, 1912.....	NF	4.7	4.1	4.4	0.2	Large.
Do.....	NF	4.7	4.0	4.3	2.0	Small.
Do.....	PP	4.7	4.8	4.7	0.6	Large.
Do.....	PP	4.7	5.1	4.9	5.5	Small.
July 29, 1910.....	PP	13.2	13.2	13.2	4.6	Large.
Do.....	PP	13.2	14.7	14.0	5.0	Medium.
Do.....	PP	13.2	17.1	15.1	-1.2	Small.
Aug. 4, 1911.....	NF	24.0	23.0	23.5	13.1	Large - size; anolyte and catholyte mixed.
Do.....	PP	24.0	23.0	23.5	12.0	Small.
Do.....	PP	28. (?)	24.0	26.0	14.2	Medium.
July 28, 1911.....	NF	24.0	25.0	24.5	14.7	Large - size; anolyte and catholyte mixed.
Do.....	PP	24.0	27.0	25.5	10.3	Small.
Do.....	PP	Lost.	34.0	22.3	Medium.
Aug. 24, 1911.....	NF	48.0	46.0	47.0	14.0	Large.
Do.....	PP	48.0	52.5	50.0	17.3	Gold cup; acid throughout.
Do.....	PP	48.0	50.0	49.0	16.8	Small; acid throughout.
Do.....	PP	48.0	44.0	46.0	17.5	Small; anode sol. neutral.
Do.....	PP	48.0	45.0	46.5	14.0	Do.
Aug. 11, 1911.....	PP	48.5	49.0	48.7	16.9	Medium.
Do.....	PP	48.5	48.0	48.2	16.3	Small.
Sept. 28, 1910.....	PP	51.6	46.2	48.9	6.7	Do.
Do.....	PP	51.6	45.6	48.6	4.7	Do.
Aug. 11, 1911.....	PP	80.0	87.0	83.0	20.0	Small; gold cup.
Do.....	PP	80.0	82.0	81.0	19.3	Small.
Do.....	PP	115.0	106.0	109.5	16.7	Do.
Do.....	PP	115.0	112.0	113.5	18.9	Do.
Sept. 7, 1911.....	NF	147.0	141.4	144.2	21.9	Large.
Do.....	PP	147.0	121.7	134.4	31.6	Small; catholyte acid; ano- lyte neutral.
Do.....	PP	147.0	132.2	139.0	43.5	Small; gold cup; catholyte acid; anolyte neutral.
Do.....	PP	202.0	180.0	191.0	39.2	Small; catholyte acid; ano- lyte neutral.
Do.....	PP	202.0	183.0	192.5	57.6	Small; gold cup; catholyte acid; anolyte neutral.

Dr. von Steinwehr in a recent article ⁸ denies that acid present in the electrolyte produces any effect on the deposit and quotes the

⁸ Zs. f. Instr., 33, p. 321; 1913.

following figures taken from the International Technical Committee's report to prove his contention:

Added acid	Deviation from normal value
5×10^{-6}	-5×10^{-5}
10×10^{-6}	-8×10^{-5}
100×10^{-6}	-12×10^{-5}
100×10^{-6}	-6×10^{-5}

If his theory were right, we should expect to find that in some cases the deposit was increased by the acid, which is not the case. It is very obvious from the above figures that acid decreases the deposit. We do not think the above data sufficient to calculate the relation between acid and decrease in deposit, and therefore have given in this paper much additional data on the subject. We will merely note here that if the above observations were plotted on the curve, Fig. 4, which we give, the first two would fall nicely on our curve. The fact that in all the cases where acid has been added to pure electrolyte 34 out of 35 cases showed a resulting decrease in deposit leaves no room for doubt that acid does decrease the deposit. Whether the law that we have derived from our observations is verified by future observers remains to be seen.

2. RESULTS OF THE POROUS POT AND SMITH NEW-FORM VOLTAMETERS

Having established the correction to be applied to the results in general for the presence of acid, we have tabulated the results obtained from the pure electrolytes having an acidity of 10 parts in 1 000 000 or less and applied to each the correction computed from the equation $y=4.5 \times x$ where y represents the change in deposit and x the mean cathode acidity, both being in parts per million.

Table 2 contains all the results with the porous-pot type of voltameter, arranged according to size of instrument. A few of the values are widely divergent from the mean, some being high and others low, but we have included all where the electrolyte conformed to our criteria of purity and no accident occurred.

Table 3, arranged similarly to Table 2, contains the results derived from Smith's form of voltameter.

In a few cases in each table the acid data are lacking or not sufficiently exact to warrant making the correction.

The total number of determinations with the Smith form was 55, from which we derive the arithmetical mean 1.01827₄, on the assumption that the variations in results between different sizes and at different times are accidental, and therefore each observation should have the same weight. Similarly, for the porous cup (156 observations) the arithmetical mean is 1.01826₇. The probable errors have been computed for a single observation and for the arithmetical mean, but the slight difference in favor of the porous-cup form we do not consider as proof of its superiority over the new form, but rather attribute it to our greater experience in using the porous-cup voltameter. This is substantiated by the fact that for the last series of observations with the large Smith form the probable error of a single observation is smaller. The slight difference in the mean results given by the two forms is just equal to the sum of the probable errors of the mean values. We give our final result as the mean of the arithmetical means with equal weight. Hence, after dropping the last figure we have as the voltage of the Weston normal cell at 20°

1.01827 VOLTS

Tables 4 and 5 give the results of the absolute determinations with the porous cup and Smith's form of voltameter for the cases in which the acidity of the electrolyte exceeded 10 parts in 1 000 000. Suitable corrections have been applied to each observation according to the formulas given on page 482. The means agree very well with the values given as the best results in the two preceding tables.

TABLE 2

Results with the Porous-Pot Form

[156 deposits. "Used electrolyte" designates that used previously]

Date	Large size				Medium size				Small size			
	Obs. value	Mean acidity	Cor-rec-tion	Cor. value	Obs. value	Mean acidity	Cor-rec-tion	Cor. value	Obs. value	Mean acidity	Cor-rec-tion	Cor. value
1910												
May 26 ⁹	1.01823	0.7	0 ₂	1.01823 ₈	1.01818 ₂	2.0	0 ₂	1.01819 ₄
26 ¹⁰	30	0.3	0 ₁	30 ₁	24	2.0	0 ₂	24 ₂
31.....	26 ₂	2.4	1 ₁	27 ₂
June 3.....	25 ₄	0.1	0 ₂	25 ₄	25 ₂	2.2	1 ₂	26 ₂
7.....	31 ₂	3.8	1 ₇	32 ₇	26 ₂	1.3	0 ₅	26 ₂
.....	24 ₂	1.6	0 ₇	25 ₂
.....	27 ₇	6.4	2 ₂	30 ₂
10.....	34 ₂	5.5	2 ₄	37 ₄	27 ₂	6.5	2 ₂	30 ₄
.....	31 ₂	6.4	2 ₂	33 ₂
14.....	31 ₇	6.7	3 ₂	34 ₇	30 ₂	6.6	3 ₂	33 ₂
.....	27 ₄	6.5	2 ₂	30 ₂
17.....	37 ₁	1.8	0 ₂	37 ₂	26 ₂	6.9	3 ₁	29 ₇
.....	34 ₇	2.2	1 ₂	35 ₇
23.....	28 ₂	0.4	0 ₂	28 ₄	31 ₂	2.8	1 ₂	32 ₂
.....	29 ₁	1.1	0 ₅	29 ₂
27.....	24 ₁	0.3	0 ₁	24 ₂	26 ₂	1.0	0 ₄	27 ₂
.....	28 ₄	0.9	0 ₄	28 ₂
30.....	25 ₇	0.3	0 ₁	25 ₂	27 ₂	1.0	0 ₄	27 ₂
.....	26 ₂	0.4	0 ₇	27 ₁	27 ₂	0.9	0 ₄	28 ₂
July 5.....	22 ₂	0.4	0 ₂	22 ₂	1.01827 ₅	0.2	0 ₁	1.01827 ₆	26 ₇	1.2	0 ₅	28 ₁
.....	25 ₂	1.5	0 ₇	26 ₂	25 ₇	0.4	0 ₂	25 ₂	26 ₄	1.2	0 ₅	26 ₂
8.....	24 ₂	0.5	0 ₂	24 ₄
.....	25 ₂	0.5	0 ₂	25 ₇
12.....	25 ₂	0.5	0 ₂	26 ₁
.....	27 ₂	0.5	0 ₇	28 ₂
15.....	23 ₁	0.1	0 ₂	23 ₁	23 ₂	0.3	0 ₁	23 ₂	23 ₇	0.6	0 ₂	24 ₂
21.....	25 ₁	0.5	0 ₂	25 ₂	26 ₂	0.5	0 ₂	27 ₁	26 ₇	0.5	0 ₂	26 ₂
29.....	27 ₂	1.0	0 ₄	28 ₂	25 ₂	0.9	0 ₄	25 ₂	20 ₂	1.5	0 ₇	21 ₂
Aug. 2.....	25 ₇	1.0	0 ₄	26 ₁	23 ₁	1.1	0 ₅	23 ₂
2 ¹¹	23 ₂	1.2	0 ₅	24 ₄
10.....	19 ₂	2.5	1 ₁	20 ₁
.....	19 ₁	2.7	1 ₂	20 ₂
18.....	25 ₇	1.7	0 ₂	26 ₂
.....	27 ₂	1.3	0 ₂	27 ₂
.....	26 ₁	1.3	0 ₂	26 ₇
.....	28 ₄	0.9	0 ₄	28 ₂
25.....	23 ₂	1.5	0 ₇	24 ₂	17 ₂	1.2	0 ₂	18 ₂	26 ₇	1.8	0 ₂	27 ₂
.....	29 ₂	2.0	0 ₂	30 ₂	19 ₂	1.9	0 ₂	20 ₄	39 ₁
.....	23 ₂	2.2	1 ₂	24 ₂	25 ₂	2.7	1 ₂	26 ₂	30 ₂	1.1	0 ₂	31 ₂

⁹ Used electrolyte.¹⁰ New electrolyte.¹¹ Used electrolyte.

TABLE 2—Continued
Results with the Porous-Pot Form—Continued

Date	Large size				Medium size				Small size			
	Obs. value	Mean acidity	Correc-tion	Cor. value	Obs. value	Mean acidity	Correc-tion	Cor. value	Obs. value	Mean acidity	Correc-tion	Cor. value
1910												
Sept. 1.....	16 ₉		0 ₀	16 ₉	15 ₆		0 ₀	15 ₆	15 ₄		0 ₀	15 ₄
									16 ₁		0 ₀	16 ₁
									16 ₉		0 ₀	16 ₉
28.....	26 ₄	0.1	0 ₀	26 ₄					22 ₀	0.3	0 ₁	22 ₁
	26 ₈	0.1	0 ₀	26 ₈					23 ₈	0.3	0 ₁	23 ₉
Oct. 11.....	22 ₁	1.0	0 ₄	22 ₉	19 ₃	1.1	0 ₅	19 ₇	29 ₁	1.4	0 ₆	29 ₇
	27 ₀	0.7	0 ₃	27 ₃					28 ₇	1.2	0 ₅	29 ₂
									22 ₃	1.1	0 ₅	22 ₇
									22 ₉	1.9	0 ₆	23 ₈
21.....	27 ₄	0.0	0 ₀	27 ₄	26 ₈	0.3	0 ₁	26 ₉	21 ₉	0.0	0 ₀	21 ₉
	23 ₃	0.3	0 ₁	23 ₃	26 ₂	0.4	0 ₂	26 ₄	19 ₃	1.0	0 ₄	19 ₈
29.....	¹² 27 ₄	1.2	0 ₈	27 ₉					29 ₀		0 ₀	29 ₀
	40 ₁	2.7	1 ₃	41 ₁					28 ₄	2.6	1 ₈	29 ₆
									29 ₃		0 ₀	29 ₃
Nov. 5.....	26 ₄	0.5	0 ₂	26 ₆					28 ₃	1.0	0 ₄	28 ₉
5.....	32 ₈	0.9	0 ₄	33 ₂					31 ₇	1.0	0 ₄	32 ₁
5.....									25 ₆	1.2	0 ₆	26 ₁
5 ¹³									27 ₀	1.2	0 ₆	27 ₅
15.....	20 ₆	1.3	0 ₆	21 ₃					25 ₃	1.9	0 ₆	26 ₂
									26 ₃	2.1	1 ₀	27 ₈
1911												
June 14.....	27 ₃	2.0	0 ₉	28 ₁					23 ₃	2.7	1 ₈	24 ₈
17.....	22 ₄	0.5	0 ₃	22 ₇					20 ₃	0.7	0 ₃	20 ₆
									22 ₀	0.7	0 ₃	22 ₃
23.....	26 ₈	0.3	0 ₁	26 ₉					26 ₆	0.6	0 ₃	27 ₃
									26 ₄		0 ₀	26 ₄
28.....	26 ₈		0 ₀	26 ₈					26 ₈	0.8	0 ₄	27 ₃
									27 ₈	0.7	0 ₃	28 ₁
July 6.....	25 ₆	0.5	0 ₃	25 ₈					26 ₈	1.0	0 ₄	27 ₀
									25 ₄	0.9	0 ₄	25 ₈
11.....	22 ₉	0.6	0 ₃	23 ₂					29 ₄	0.9	0 ₄	29 ₈
									29 ₂	1.0	0 ₄	29 ₆
17.....	25 ₈	0.6	0 ₃	25 ₉					27 ₇	1.6	0 ₇	28 ₄
28.....					29 ₈	1.3	0 ₆	30 ₄	24 ₄	1.3	0 ₆	25 ₀
Aug. 4.....					30 ₀	0.6	0 ₃	30 ₃	26 ₁	0.7	0 ₃	26 ₄
11.....					27 ₀	1.2	0 ₅	27 ₃	¹⁴ [19 ₃]		0 ₀	
24.....									22 ₃	0.3	0 ₁	22 ₃
									27 ₆	0.3	0 ₁	27 ₇
Sept. 7.....									31 ₇	1.9	0 ₉	32 ₈
									33 ₀	2.0	0 ₉	33 ₉

¹³ Acidity for large one is final.¹³ Used electrolyte.¹⁴ Accident to bracketed observation.

TABLE 2—Continued

Results with the Porous-Pot Form—Continued

Date	Large size				Medium size				Small size			
	Obs. value	Mean acid- ity	Cor- rec- tion	Cor. value	Obs. value	Mean acid- ity	Cor- rec- tion	Cor. value	Obs. value	Mean acid- ity	Cor- rec- tion	Cor. value
1911												
Oct. 21									26 ₁		0 ₀	26 ₁
									28 ₀		0 ₀	28 ₀
26									22 ₀	3.8	1 ₇	24 ₆
									26 ₉	4.0	1 ₈	28 ₇
Nov. 9									29 ₁		0 ₀	29 ₁
									28 ₆	0.4	0 ₅	28 ₆
16	31 ₂	0.1	0 ₀	31 ₂	29 ₂		0 ₀	29 ₃	30 ₅	0.1	0 ₆	30 ₅
									29 ₀	1.1	0 ₅	29 ₆
22	32 ₈	0.0	0 ₀	32 ₈					27 ₇	0.4	0 ₈	27 ₉
Dec. 4	26 ₈	0.8	0 ₄	27 ₀					21 ₂	1.6	0 ₇	21 ₉
1912												
Jan. 16	26 ₉	2.0	0 ₉	27 ₈					28 ₄	1.9	0 ₆	29 ₈
Feb. 13	27 ₆	0.0	0 ₀	27 ₅					24 ₃	0.5	0 ₈	24 ₆
20	27 ₂	0.0	0 ₆	27 ₃					24 ₆	0.1	0 ₀	24 ₆
	26 ₇	4.7	2 ₁	28 ₈					19 ₁	4.9	2 ₁	21 ₃
Mar. 12	29 ₆	0.7	0 ₅	29 ₈					21 ₇	0.5	0 ₅	21 ₉
									25 ₈	0.4	0 ₃	26 ₀
Mean	1.01826 ₉		0 ₅	1.01827 ₄	1.01824 ₄		0 ₄	1.01824 ₈	1.01826 ₀		0 ₇	1.01826 ₇

Mean of all, 1.01826₇; average deviation, 3₀; probable error of single observation, 2₅; probable error of final result, 0₂.

TABLE 3
Results with Smith's Form.
[55 deposits]

Date	Large size				Medium size				Small size			
	Obs. value	Mean acidity	Correc- tion	Cor. value	Obs. value	Mean acidity	Correc- tion	Cor. value	Obs. value	Mean acidity	Correc- tion	Cor. value
1910												
May 31.....	1.01820 ₈	0.2	0 ₁	1.01820 ₉
	25 ₂	0.2	0 ₁	25 ₃
June 3.....	23 ₈	0.0	0 ₀	23 ₈	1.01828 ₉	0.3	0 ₁	1.01829 ₀
7.....	23 ₄	3.8	1 ₇	25 ₁	18 ₂	4.0	1 ₈	20 ₀
10.....	22 ₂	4.8	2 ₂	25 ₁	20 ₄	5.1	2 ₃	22 ₇
14.....	20 ₆	6.2	2 ₈	23 ₇	16 ₇	5.9	2 ₇	19 ₄
17.....	22 ₂	1.5	0 ₇	22 ₂	18 ₃	1.7	0 ₈	19 ₁
23.....	32 ₆	0.3	0 ₁	32 ₇	35 ₈	0.1	0 ₀	35 ₆
27.....	24 ₈	0.2	0 ₁	24 ₉
Sept. 1.....	19 ₆	0 ₀	19 ₆	26 ₉	0 ₀	26 ₇
28.....	20 ₇	0.0	0 ₀	20 ₇
Oct. 11.....	26 ₉	0.9	0 ₄	27 ₂	29 ₁	0.9	0 ₄	29 ₅
29.....	23 ₂	0 ₀	23 ₂
Nov. 5.....	33 ₂	0.4	0 ₂	33 ₀
15 ¹⁶	25 ₁	1.5	0 ₇	25 ₈
1911												
June 14.....	30 ₆	2.0	0 ₆	31 ₅	40 ₄	0 ₀	40 ₄
17.....	35 ₂	0.5	0 ₂	35 ₄	37 ₄	0.5	0 ₂	37 ₆
23.....	30 ₆	0.3	0 ₁	30 ₇	29 ₄	0.3	0 ₁	29 ₅
28.....	24 ₂	0 ₀	24 ₂	28 ₀	0 ₀	28 ₀
July 6.....	27 ₆	0.5	0 ₂	27 ₈	29 ₆	0.4	0 ₂	29 ₈
11.....	22 ₂	0.3	0 ₁	23 ₀	25 ₂	0.2	0 ₁	25 ₃
28.....	25 ₀	0.8	0 ₄	25 ₄
Aug. 4.....	31 ₁	0.3	0 ₁	31 ₂
24.....	23 ₅	0.5	0 ₂	23 ₇
Sept. 7.....	33 ₀	1.3	0 ₆	33 ₆
Nov. 16 ¹⁶	28 ₆	0.0	0 ₀	28 ₆	28 ₈	0 ₀	28 ₈
22.....	29 ₄	0 ₀	29 ₄
1912												
Jan. 16.....	30 ₁	1.7	0 ₈	30 ₉	1.01831 ₁	1.7	0 ₈	1.01831 ₉
Feb. 13.....	28 ₇	0.0	0 ₀	28 ₇	33 ₃	0.0	0 ₀	33 ₃
20.....	28 ₈	0 ₀	28 ₈	29 ₇	0 ₀	29 ₇
	28 ₆	4.4	2 ₀	28 ₆	27 ₇	4.3	1 ₉	29 ₆
28.....	20 ₂	0.8	0 ₄	20 ₆	21 ₆	0.8	0 ₄	22 ₀
	21 ₆	0.8	0 ₄	22 ₀
Mar. 12.....	30 ₅	0 ₀	30 ₅	31 ₉	0 ₀	31 ₉
Mean.....	1.01826 ₃	0 ₅	1.01826 ₃	1.01827 ₅	0 ₅	1.01828 ₀	1.01830 ₄	0 ₄	1.01830 ₈

Mean of all, 1.01827₄; average deviation, 4₀; probable error of single observation, 3₄; probable error of final result, 0₅.

¹⁶ Used electrolyte.

¹⁶ 20 per cent electrolyte.

TABLE 4

Results with the Porous-Pot Form

HIGH ACIDITIES

Date	Large size				Medium size				Small size			
	Observed value	Mean acidity	Correc-tion	Cor-rect value	Observed value	Mean acidity	Correc-tion	Cor-rect value	Observed value	Mean acidity	Correc-tion	Cor-rect value
1910												
July 29.....	1.01823 ₂	13.2	5 ₉	1.01829 ₁	1.01820 ₅	13.9	6 ₀	1.01826 ₅	1.01821 ₆	15.0	6 ₆	1.01828 ₂
Sept. 28.....									16 ₁	48.9	17 ₄	33 ₅
									18 ₂	48.6	17 ₃	35 ₅
1911												
July 28.....					07 ₁	34	13 ₂	20 ₃	13 ₃	25.5	10 ₄	24 ₃
Aug. 4.....					15 ₃	26	10 ₆	26 ₄	13 ₃	23.5	9 ₈	23 ₇
11.....					09 ₃	48.7	17 ₃	27 ₁	10 ₅	48.2	17 ₂	27 ₇
									07 ₃	50.2	17 ₇	25 ₅
									07 ₃	49	17 ₄	24 ₇
									07 ₁	46	16 ₆	23 ₇
									10 ₆	46.5	16 ₃	27 ₄
Mean.....	1.01823 ₂		5 ₉	1.01829 ₁	1.01813 ₃		11 ₃	1.01825 ₁	1.01812 ₇		14 ₇	1.01827 ₄

Mean of all 1.01826₅.

VERY HIGH ACIDITIES

1911												
Aug. 11.....									1.01806 ₆	83.5	23 ₇	1.01830 ₃
									07 ₃	81	23 ₄	30 ₇
									10 ₆	109.5	26 ₈	36 ₃
									07 ₃	113.5	27 ₇	35 ₅
Sept. 7.....									1.01787 ₂	139.8	29 ₃	17 ₄
									1.01800 ₁	134.5	29 ₀	29 ₁
									1.01791 ₃	192	33 ₃	24 ₉
									1.01773 ₃	193.7	33 ₇	07 ₂
Mean.....											28 ₀	1.01826 ₅

TABLE 5

Results with the Smith Form

[High acidities in large size only]

Date	Observed value	Mean acidity	Correc- tion	Correct value
July 28.....	1.01810 ₀	24.5	10 ₁	1.01820 ₁
Aug. 4.....	17 ₈	23.5	9 ₈	27 ₆
24.....	09 ₃	47	16 ₉	26 ₉
Sept. 7.....	10 ₇	144.4	29 ₉	40 ₆
Mean.....	1.01811 ₉	16 ₇	1.01828 ₆

3. RESULTS OF OTHER FORMS OF VOLTAMETERS

Table 6 contains the summary of results with the siphon voltameter, the modified siphon, and the Poggendorff forms. These results we do not regard as sufficiently accurate to include in the mean with the porous cup and Smith's form. The figures given for the siphon form are relative only, since it is not possible to maintain the current constant during the experiment, owing to the heating of the long column of electrolyte in the siphon. The modified siphon and the Poggendorff form present too great difficulties with the anode slime to be perfectly reliable. The mean of these 21 observations is 1.01832 volts, which although appearing much higher than the mean value found with the porous cup and Smith forms when using six figures is very near to the value adopted by the International Technical Committee (1.0183), as the voltage of the Weston normal cell at 20° C when we use five figures only. We now have five different forms of voltameter, giving results that fix the value to 1 in 10 000 quite certainly. We think that the reason these latter forms give higher values is the escape of anode slime to the cathode in the case of the modified siphon and Poggendorff forms. We are not clear why the siphon form generally gives results a little larger than the porous cup and Smith's forms.

TABLE 6

Results with other Forms of Voltameter

[Acidities small; no corrections made]

Date.	Siphon form ¹⁷			Modified siphon	Poggendorff form
	Large	Medium	Small		
1910					
May 26.....					1.01829
31.....					23
June 3.....					32 ₀
17.....					24 ₃
23.....					26 ₄
27.....				1.01832 ₅	40 ₈
30.....				29 ₃	31 ₄
1911					31 ₈
June 17.....				49 ₄	28 ₉
23.....				40 ₆	
28.....				32 ₃	
July 6.....				32 ₂	
11.....				36 ₄	
1912					
Jan. 22.....	1.01837 ₇	(1.01859) ₉	1.01837 ₂		
30.....	30 ₆	26 ₇	30 ₇		
Mean.....	1.01834 ₁	1.01826 ₇	1.01833 ₆	1.01834 ₆	1.01829 ₇

Arithmetical mean: Siphon form, 1.01832₄; modified siphon form, 1.01834₆; Poggendorff form, 1.01829₇; mean (21 observations), 1.01832.

¹⁷ Relative experiments.

4. MISCELLANEOUS RESULTS

Table 7 contains the results of the miscellaneous series of deposits in most of which the electrolyte was not pure and in some cases having been purposely contaminated for the sake of experiment. The several samples of salt as purchased could not be used for the higher precision work without further purification.

The salt from Poulenc, which was left with us by Prof. Laporte of the Laboratoire Central d'Électricité, was good in its original condition and was not improved by the simple means taken to purify it, while on the other hand, the Baird and Tatlock triple crystallized salt used July 17 was very bad in its original condition.

A single fusion, however, followed by a surface washing of the fused cake made it satisfactory, and it was repeatedly used in this way. The difference between the two salts is probably due to different impurities, although in the case of the Poulenc salt we did not have enough at our disposal to make the tests conclusive.

TABLE 7

Miscellaneous Deposits not Including the Experiments on the Effect of Acid

[The results recorded in this table are explained in the column of remarks. With a few exceptions, which are noted, they have not been included in the tables of best results]

Date	Large	Small	Remarks
1910			
July 8.....	1. 01836 ₃	1. 01827 ₆	Salt from Poulenc, recrystallized once and fused
	39 ₂	29 ₂	Salt from Poulenc, recrystallized once but not fused
12.....	1. 01835 ₈	1. 01824 ₉	Salt from Poulenc, fused but not recrystallized
	30 ₄	24 ₄	Salt from Poulenc, not fused and not recrystallized
Aug. 2.....	1. 02095	1. 02046	Filter paper extract added to electrolyte, neutral, very heavily striated
	074	040	Filter paper extract added to electrolyte, 10×10^{-6} acid very heavily striated
Aug. 10.....	1. 01840 ₅	1. 01829 ₃	Salt from Baker as purchased, KMnO_4 test not satisfactory
	39 ₁	27 ₄	Do.
18.....		1. 01825 ₇	18 per cent pure electrolyte, included in mean of Table 2
		27 ₂	15 per cent pure electrolyte, included in mean of Table 2
		26 ₁	10 per cent pure electrolyte, included in mean of Table 2
		28 ₄	7 per cent pure electrolyte, included in mean of Table 2
22.....	8208.92		Milligrams, Septum a filter tube especially treated, electrolyte acid
	.50		Milligrams, Septum a filter tube especially treated, electrolyte neutral
Nov. 15.....	1. 01829 ₆	1. 01824 ₈	0.1 per cent of KNO_3 was added to the electrolyte
23.....	1. 01852 ₁	1. 01839 ₂	Baird and Tatlock electrolyte as purchased
		39 ₂	Do.
		35 ₅	Furfural, not polymerized, 5 in 10^{-5} parts added to electrolyte
		35 ₈	Do.
		1. 02182	Deposit made in an atmosphere of CO_2
		88	Do.
1911			
July 17.....	1. 01854 ₈	1. 01845 ₅	Baird and Tatlock electrolyte as purchased, porous cup voltmeter
	73 ₁	67 ₂	Baird and Tatlock electrolyte as purchased, Smith form
Oct. 21.....		1. 01822 ₃	American made porous pot, coarse and thick
		19 ₆	Do.
		35 ₈	Pukal filter bulbs used as septum
		25 ₉	Do.
26.....		1. 01821 ₉	American porous pots, same as on Oct. 21
		21 ₁	Do.
		38 ₂	Pukal filter bulbs, same as on Oct. 21
		36 ₁	Do.

TABLE 7—Continued

Miscellaneous Deposits not Including the Experiments on the Effect of
Acid—Continued

Date	Large	Small	Remarks
1911			
Nov. 9.....		1. 01825 ₉	American porous pots after especial efforts to put them in suitable condition
		27 ₆	Do.
		32 ₈	Pukal filter bulbs after especial efforts to put them in suitable condition
		32 ₈	Do.
27.....		1. 01831 ₁	Piece of hard rubber suspended in the electrolyte, medium size
		32 ₁	20 per cent electrolyte with 2×10^{-6} alkali added
Dec. 4.....	1. 01828 ₈		Piece of hard rubber suspended in the electrolyte
		1. 01826 ₈	2×10^{-6} Ba(OH) ₂ added to the electrolyte
		26 ₈	2.5×10^{-6} NaOH added to the electrolyte
14.....	1. 01842 ₃		Smith form. The electrolyte was not completely freed from silica from long storage in glass bottles
	44 ₇	1. 01839 ₆	Do.
		37 ₂	Porous cup. The electrolyte was not completely freed from silica from long storage in glass bottles
		30 ₁	Do.
1912			
Jan. 16.....	1. 01836 ₇	1. 01828 ₄	Second trial of the electrolyte of Dec. 14, porous-cup form
Feb. 28.....	1. 01838 ₄	1. 01826 ₆	Another electrolyte like Dec. 14 satisfying the KMnO ₄ test but shows volume effect
		27 ₀	Do.
Mar. 1.....	1. 01937 ₃		Electrolyte strongly contaminated with filter paper; deposit made for analysis

The deposits on August 18 are included in this table merely to draw attention to the fact that the variation in the concentration of the electrolyte is without any certain effect on the deposited silver. These deposits were perfectly normal and have been included in the results given in Table 2. The deposits made November 23 in an atmosphere of CO₂ show a great increase in the mass of deposit. They were strongly striated and so tightly adherent that it was impossible to loosen any of the silver with a glass rod.

Beginning on October 21 we made several experiments on porous pots other than the particular kind that we have adopted for this

work. The kind which we have designated in the table as "American made" were purchased in 1907. They are slightly conical in shape and somewhat thicker and coarser than the kind we generally use. They have the added disadvantage of containing considerable quantities of iron. In the first two experiments some difficulty was experienced in getting the cups in proper condition, as the electrolyte at the end of each experiment was decidedly acid. In the third (Nov. 9), however, the conditions were better and the weight of deposit normal. The Pukal bulbs gave consistently high values, although they are made, presumably, of the same material as our best porous cups. The cause of this is not certainly known, but owing to the smallness of the anode that must be used, because of the narrow neck of the bulb, some trouble might perhaps be expected, and such bulbs should not be used. Our results are too few in number to settle the question definitely. The tests made with hard rubber in the electrolyte were for the purpose of showing whether or not the hard rubber friction rings which we have used to support the porous cups were likely to produce errors owing to the electrolyte creeping up the sides of the porous cups by capillary action and in this way wetting the rubber. Jaeger and Von Steinwehr have actually immersed the rubber in the electrolyte as a support for the porous cup. Our results show that this is probably permissible, though as a matter of precaution we think that such foreign substances should be kept out of the electrolyte as far as possible.

Two electrolytes are quoted as showing a volume effect although they satisfied the permanganate test. This may be due to the presence of some such colloid as silica from too long storage in glass containers (Part III, p. 543), which would not affect the KMnO_4 test but may increase the deposit. This case is the exception rather than the rule and does not invalidate the value of the KMnO_4 test, if proper precautions are taken when preserving the electrolyte in glass. We think, however, that the possibility of this case arising emphasizes the necessity of specifying the volume test also as one of the criteria for the purity of the electrolyte.

III. SPECIAL INVESTIGATIONS

A. ON THE AGREEMENT OF VARIOUS FORMS

1. COMPARATIVE RESULTS

At various times during the course of the work relatively large differences have appeared between the porous-cup form of vol-
tameter and Smith's new form, but in general it has not been
possible to find the cause of the difference, although numerous
attempts have been made to do so. This is because the difference
has usually almost vanished, the two forms drawing together as the
investigation proceeded. The results given in Tables 2 and 3
show the average difference between the two forms to be only 7
in 1 000 000, which is sufficiently good agreement for a primary
standard at the present time. Comparing the values of the present
paper (3d series), taken in groups at different periods of the work,
we find the agreement to be in general very good. The results
are thus shown in Table 8. Table 9 shows the values obtained
from these two forms at different periods, dating back to the
beginning of the Bureau's investigation.

TABLE 8

Mean Values for Weston Cell at Different Periods of the Work

Date	Smith form						Porous-pot form					
	No.	Large	No.	Medium	No.	Small	No.	Large	No.	Medium	No.	Small
May 26 to Sept. 1, 1910.....	10	1. 01824 ₄	7	1. 01824 ₇	21	1. 01827 ₃	15	1. 01823 ₇	36	1. 01826 ₉
Sept. 28 to Nov. 23, 1910.....	4	1. 01827 ₅	2	1. 01825 ₁	11	1. 01827 ₇	3	1. 01824 ₃	17	1. 01826 ₄
June 14, 1911, to Mar. 12, 1912.	18	1. 01828 ₁	12	1. 01830 ₅	2	1. 01830 ₈	15	1. 01827 ₄	4	1. 01829 ₄	34	1. 01826 ₇
Means according to size ..	32	1. 01826 ₈	21	1. 01828 ₉	2	1. 01830 ₈	47	1. 01827 ₄	22	1. 01824 ₈	87	1. 01826 ₇

Date	Mean according to form				Mean of both	
	No.	Smith	No.	Porous pot	No.	
May 26 to Sept. 1, 1910.....	17	1. 01824 ₆	72	1. 01826 ₃	89	1. 01825 ₅
Sept. 28 to Nov. 23, 1910.....	6	1. 01826 ₇	31	1. 01826 ₇	37	1. 01826 ₇
June 14, 1911, to Mar. 12, 1912.....	32	1. 01829 ₁	53	1. 01827 ₁	85	1. 01828 ₁

TABLE 9

Comparison of Recent Values for the Weston Normal Cell

Date	Observations	Voltameter	Deposits	Value for cell
1908-9....	First series, Bureau of Standards.....	Porous cup.....	42	1.01828 ₇
1909-10...	Second series, Bureau of Standards.....	Small porous cup.....	44	1.01827 ₅
1910.....	International Technical Committee.....	Porous cup.....	14	1.01828 ₆
1910.....	do.....	Smith's form.....	8	1.01828 ₇
1910.....	Smith and Vinal at Teddington.....	Porous cup.....	15	1.01821 ₈
1910.....	do.....	Smith's form.....	19	1.01830 ₄
1911-12...	Third series, Bureau of Standards.....	Porous cup.....	156	1.01826 ₇
1911-12...	do.....	Smith's form.....	55	1.01827 ₄

Mean of 271 determinations, porous cup, 1.01827₆; mean of 82 determinations, Smith's form, 1.01828₂.

2. POSSIBLE EXPLANATIONS OF OBSERVED DIFFERENCES

Notwithstanding the fact that the difference between the final average values of the two forms of voltameters is only seven parts in 1 000 000 (Tables 2 and 3), there is reason for believing that this is not accidental, but on the contrary is due to causes that are persistent. We have given much study to the cause of this difference as well as to the differences between the different sizes of voltameters of each form, and present the following discussion of the possible causes of the small differences.

First. The data on acidity show that if neutral electrolyte is employed the acidity of the cathode electrolyte at the conclusion of the experiment is on the average higher by a few parts in a million in the porous-pot form than in the Smith form. This circumstance may account in part at least for the lower values obtained in the former type, since the effect of acid upon the deposit from a pure electrolyte is to decrease it slightly.

On the other hand, it is quite as certain that the very concentrated electrolyte formed around the anode in both forms of voltameters may become very slightly basic. In view of the fact that in three of the deposits made by the International Technical Committee (report, pp. 157-158) a few parts per million of added base caused a heavy striated deposit, it seems possible that this base formed around the anode may be another cause of the difference between the two forms. It is to be noted in this connection, however, that the basic anode electrolyte formed in the voltameter is

not opalescent and therefore the silver hydroxide is probably not colloidal, so that its effect is doubtless not nearly so pronounced as in the case of the added base. Nevertheless, there is a possibility of the formation of colloidal hydroxide at the cathode if any of the anode solution reaches the layer of dilute electrolyte next the cathode; for it is known that silver hydroxide is much less soluble in dilute than in concentrated silver nitrate solution.

It is known also that colloidal silver hydroxide may remain undissolved in presence of more than its equivalent amount of nitric acid. Therefore the possibility that nitric acid may be found at the cathode equivalent in amount to the base formed at the anode does not vitally affect the question of the formation of colloidal silver hydroxide near the cathode.

Second. In the paper recently published by Washburn and Bates¹⁸ they emphasize the reversibility of the iodine voltameter, and it was with a view to ascertaining the limits within which the silver voltameter might be said to be reversible that we undertook a series of measurements described in this paper under the head of "Reversibility." One fact was noted in these experiments which offers the second possible explanation of the differences between the porous cup and new form of voltameter and also why the small sizes of new form voltameter should give heavier deposits than the larger size.

The anodes in the experiment of March 11 were two large size bowls, one containing a pure crystalline deposit and the other strongly striated, each being about 10 grams. These bowls were connected to smaller bowls, serving as cathodes, by glass siphons. The electrolyte in both was made from pure salt. The current passed through them was one-half ampere for one hour, thus transferring about 2 grams of silver from the large bowls to the small ones. At the conclusion of the run the voltameters were carefully dismantled and both anode and cathode bowls carefully washed, dried, and weighed. The quantitative results are not of interest here, but only the fact that the conditions found in the two anode bowls were radically different. That which contained the pure silver deposit was white and contained relatively little anode slime. This too was white and fairly coarse so that it did not

¹⁸ J. Am. Chem. Soc., **34**, p. 1341; 1912.

present any serious difficulty in the washing of the bowl. On the other hand, the cup containing the striated deposit was very dark in color and contained a very large quantity of slime which made much trouble in the washing. The only practical method of collecting this without filtering the requisite four or five liters of wash water through a small quantitative filter paper was found to be an hourly examination of the water in large beakers, collecting each time the sediment as it slowly settled to the bottom. After the first large amount had been collected and returned to the bowl, the wash water was apparently perfectly clear, but considerable quantities of fine brownish slime could be collected at each time that the liquid was examined.

The bearing which this fact has upon the difference between the Smith form and the porous cup consists in emphasizing the necessity of using pure electrolyte in forming the anode for the former. In general no great pains have been taken as to the purity of the solution used in the preparation of the anodes, and past experience has shown that the amounts of slime seen on the anode in the Smith form varied considerably without any definite reason being known. It is easily conceivable that some of the invisible slime which took 24 hours to settle out of the wash waters may have exercised some influence in increasing the deposit in the new form over the porous-cup form, since in the latter it could not pass through the porous cup. This would also explain why the small Smith form gives larger deposits generally than the large size, since obviously the same amount of slime would probably be formed in the two sizes when run in series, the anodes being alike, and the effect would be proportionately greater in the smaller volume of solution. This also may explain why the difference between the two forms has varied somewhat at different times, since if this theory is correct the difference would depend to some extent at least on the electrolyte used for forming the anode. The hopeful fact remains, however, that there is little evidence of trouble with the Smith form if the anode is formed in pure electrolyte. It is of course possible to put this theory to a crucial test and such was planned, but the urgency of other work prevented more than one experiment being made. Hence we can not lay much emphasis on

the result obtained, although it is in the right direction according to the theory.

Form	Anode	Deposit	Difference
New form, large.	Prepared from impure electrolyte	4231. 87	} 3 parts in 100 000
	Prepared from pure electrolyte	4231. 75	

Other observations on the effect of impure anodes are given under the head of "Reversibility of the voltameter," page 523.

B. ON THE ACCURACY OF THE MEASUREMENTS

We have given at the end of Tables 2 and 3 a statement of the probable error of a single measurement and also of the probable error of the arithmetical means. Since the probable error of the means is equal to the probable error of a single observation divided by the square root of the number of observations we may readily find by putting the probable error of the final result equal to some arbitrary figure, as, for example, 1 part in 100 000 that if the probable error of a single observation is 3.4 parts in 100 000 as in the case of the Smith form that the number of observations required is 12 and similarly for the porous pot 7 observations, which, however, must be independent in the sense that each result is the result of a different experiment and on the assumption that the accidental errors are of the same magnitude as in the present work. From the above it would appear that somewhat better agreement might be expected in the results recorded in Table 9 if the errors entering were purely accidental, which is certainly not the case. Perhaps the chief error arises from a variation in the electrolyte.

We know that the electrolyte used in the first two series of experiments was not as pure as in the last and therefore we have selected out the small size porous-cup voltameters as being the more accurate for reasons which we have given in connection with the volume effect. It is to be expected then that these results should be somewhat above the average. The most notable exceptions are the results obtained by Smith and Vinal at Teddington for which no satisfactory explanation has been found. For the

last series the results are based on the determinations with what we believe to have been the purest salt and are probably the most trustworthy.

In making determinations in the future for checking the constancy of the Weston normal cell we believe that as many different samples as possible of AgNO_3 , each conforming to the required standard of purity, should be used to avoid systematic errors.

One further possible source of error remains to be mentioned. We have been dependent on wire standards for our value of the ohm and we have endeavored to conform always to the same basis. It is, however, possible that a slight drift may have taken place during the years that have been consumed in this investigation. Similarly there is an uncertainty as to how nearly the cells measured represent the Weston normal cell. However, these uncertainties are probably less than one part in a hundred thousand, and for want of any knowledge as to their magnitude no correction can be applied.

C. RELIABILITY OF IODEOSINE AS AN INDICATOR

In the previous paper of this series (this Bulletin, 9, p. 529) a method was described for the determination of small amounts of free acid or alkali with an accuracy of at least 1 part per 1 000 000. In order to obtain such a degree of accuracy it can be shown that an indicator must be selected, the turning point of which is below $[\text{H}^+] = 10^{-5}$, i. e., the indicator must be sufficiently sensitive to detect free nitric acid if the latter is hundred-thousandth normal ($0.00001 \text{ N HNO}_3 = 0.63 \text{ parts HNO}_3 \text{ per } 1\,000\,000$). In order to determine whether iodeosine as used in the method described possesses this degree of sensibility, tests were made in which solutions of pure potassium chloride and nitrate were titrated after the addition of known small amounts of acid or alkali, using both iodeosine and methyl red as indicators. In every case the results with these two indicators agreed within 0.05 cc of 0.001 N acid, equivalent to about 0.3 part per 1 000 000 of nitric acid. In general it was found that methyl red was nearly as sensitive as iodeosine and for an accuracy of 1 part per 1 000 000 could be substituted for it in these titrations. In using methyl red as the indicator, about one drop of the indicator

solution (0.2 per cent in alcohol) is added to 10 cc of the solution to be tested and the titration carried out directly in a small flask or beaker, the operation therefore being much more convenient than when iodeosine is used. The conclusion of Tizard¹⁹ that methyl red changes at about 10^{-6} was confirmed by experiments with a hydrogen electrode, using solutions of potassium chloride, the reaction of which was changed by the addition of known amounts of 0.001 N acid or alkali. While such a method is not suitable for the very accurate preparation of solutions of known hydrogen ion concentration, it obviated possible effects of foreign salts, since the solution used with the hydrogen electrode was similar to that present in the titrations.

Since the iodeosine, under the conditions used, was found to be slightly more sensitive to acid than the methyl red, it follows that the iodeosine has effectively a turning point below $[H^+] = 10^{-6}$ and is therefore suitable for detecting as little as 1 part in 1 000 000 of free acid or alkali. As the exact turning point of the iodeosine is no doubt dependent upon the concentration of the iodeosine in the ether solution and aqueous phases, the above conclusion only applies with certainty to titrations carried out under approximately the conditions recommended in the method as described. For the comparisons of these indicators with the hydrogen electrode we are indebted to Dr. William Blum, of this Bureau.

D. EFFECT OF ACID

We have given above a discussion of the effect of acid in the electrolyte on the deposit of silver and have shown that when the electrolyte is pure the silver deposit is less than normal, depending on the amount of the acid present. We purposely limited the discussion at that point to the case of pure electrolytes, since we wished to derive a correction to be applied to the observations in our tables of best quantitative measurements where only pure salt was used.

1. EFFECT ON IMPURE SOLUTIONS

When acid is added to solutions that are impure the effect can not be predicted, since it depends on the nature of the impurity. The following experiments show a case where an electrolyte

¹⁹ J. Chem. Soc., 97, pp. 2477-2490, 1910.

believed to be pure and yielding satisfactory results in the voltmeter was made to show a pronounced volume effect by the addition of a small amount of pure nitric acid.*

TABLE 10

[Using porous-cup voltmeters]

Date	Neutral electrolyte		Acid electrolyte		Size bowl
	Value	Mean acidity	Value	Mean acidity	
		pts. in 10^6		pts. in 10^6	
July 15, 1910.....	1. 01823 ₁	0. 1	1. 01832 ₁	9. 3	Large
	1. 01823 ₆	0. 3	1. 01822 ₃	10. 3	Medium
	1. 01824 ₀	0. 6	1. 01818 ₈	9. 9	Small
July 21, 1910.....	1. 01825 ₃	0. 5	1. 01824 ₆	10. 2	Large
	1. 01827 ₁	0. 5	1. 01820 ₀	9. 9	Medium
	1. 01826 ₉	0. 5	1. 01819 ₄	9. 9	Small

On the other hand, the experiment of August 2 showed that the addition of acid to electrolyte containing considerable filter paper extract might produce the opposite effect. Using two large and two small porous-cup voltmeters with enough filter paper extract added to the electrolyte to produce a very high value for the cell we found the following results:

Size	Neutral electrolyte	Acid electrolyte
Large.....	1. 02095	1. 02074
Small.....	1. 02046	1. 02040

The terms acid and neutral electrolyte used in connection with so contaminated a solution are merely relative, since the acidity of the solution changes so fast when thus contaminated that exact measurements are not possible. (See p. 247, Pt. II, of this series of papers, this Bulletin, vol. 9.) The acid added in this experiment would have been sufficient to render a pure solution acid by 10×10^{-6} parts.

Continuing this line of work, we next tried a very resistant cellulose. In this experiment two filter tubes that had been washed with hot distilled water to dissolve the soluble celluloses were used

* The presence of an impurity in this silver nitrate was later confirmed by the permanganate test.

in two large Rayleigh voltameters. They were assembled the night before the experiment with the purest electrolyte, and nitric acid to make the electrolyte 30×10^{-6} parts acid was added to one. At the conclusion of the experiment there was only 15×10^{-6} parts acid found in this voltameter. The resulting deposits were as follows: From neutral electrolyte, 8208.50 mg; from acid electrolyte, 8208.92 mg.

The result would seem to show that the acid broke up the resistant cellulose into reducing agents and thereby caused heavier deposits.

It is quite apparent from these experiments that the effect of acid in impure solutions is uncertain and we think that enough has been said to indicate that acid may sometimes increase the deposit, as in the experiment of July 15. Smith²⁰ concludes that the effect of nitric acid is to lower the deposit but notes that the effects are very irregular, in some cases a marked increase resulting. We think that the phenomena he observed are explained by the variations in the purity of the electrolyte.

2. NATURE OF THE ACTION OF ACID

To explain why the acid lowers the deposit when added to pure electrolyte is very difficult and in spite of numerous qualitative experiments no certain explanation has as yet been found. Leduc²¹ has given much attention to this question; he, however, thinks that when acid is formed in the voltameter it originates at the anode, but this seems doubtful from our experiments as we shall show later. It is of course possible that the hydrogen migrating to the cathode may take part in secondary reactions, but the experimental difficulties in obtaining definite data as to what these may be are very great. We have tried experiments of letting acid in water solutions of known strength stand on silver deposits without the passage of electric current and have estimated the silver dissolved by careful titrations with ammonium thiocyanate. The amounts found, however, were very small even for acid of normal strength standing over night and the results showed the surface condition of the silver to be the impor-

²⁰ Phil. Trans. A 207, p. 594; 1908.

²¹ J. de Physique I, p. 561; 1902.

tant thing rather than the amount of acid or the length of time of contact. No conclusion can therefore be drawn as to whether there is a possible corrosion of the cathode deposit or not.

In another direction, however, we could fortunately get definite and satisfactory results.

It seemed possible that in the case of an electrolyte which was appreciably acid the decrease in the silver deposit might be due to a depositing out of the hydrogen ions before the silver begins to deposit since there is probably at the instant the current begins to flow a greater difference of potential at the cathode than obtains afterwards, as the discontinuous character of the deposit indicates that the potential difference must break through a sort of surface film and establish outlets²² for the current to the platinum cathode. If this were possible, by making deposits of about 1 milligram each from solutions containing acid and without the difference ought to be quite apparent.

The deposits were all made in large size bowls with the acidity of the electrolyte carefully determined. The time of the deposit and the current used were varied, but always made to yield about 1 milligram of silver theoretically. The time was measured by a chronograph, except for the longest run, and the current by a millammeter. Following this the deposits were carefully washed. To determine the amounts of silver deposited several methods were tried since the weighing of so small a deposit was unduly laborious. Experiments with the nephelometer showed that the precipitate of silver chloride formed after the deposits had been dissolved out of the cups with nitric acid were too heavy to use this instrument with satisfaction. In the end it was found best to use a $\frac{N}{1000}$ solution of ammonium thiocyanate with ferric ammonium alum as the indicator after the titrating solution had been standardized with a standard silver solution. By this means very satisfactory results were obtained. The silver deposits were removed from the bowls by hot HNO_3 and water 1:3.

The results are given in the following table, together with the results of several similar experiments in which the cups were first electrolyzed for four hours to fill them with oxygen or hydro-

²² See *The Silver Voltameter*, Part II, this Bulletin, 9, p. 278 (Reprint 195).

gen. In this case there appears to be a decrease in the deposit in the oxygenated cup that did not appear again after the first time it was used. The effect of oxygen in the cup thus appears to be smaller than has been previously supposed. The slight gain in the hydrogenated cup is not readily explainable. The titrations are estimated to be good to about 0.05 milligram of silver. The result of these experiments is to show pretty certainly that the presence of acid does not cause the diminution of the deposit by a preliminary deposition of hydrogen before the silver begins to deposit. Except for eliminating this possible explanation, however, it throws no light on the mechanism of the effect of acid.

TABLE 11

Experiments to Determine the Initial Effect of Acid, and Oxygen and Hydrogen

Date	Cup	Acidity of electrolyte	Current	Time	Calculated deposit	Observed deposit	Remarks
1912			amps	sec	mg	mg	
Dec. 14	93	11×10 ⁻⁶ acid.....	.040	25.0	1.118	1.13	Deposit almost invisible
	95	Neutral.....	.040	25.0	1.118	1.13	Do.
15	93	11×10 ⁻⁶ acid.....	.0000069	147060.	1.13	1.10	Deposit consisted of 13 crystals in each cup
	95	Neutral.....	.0000069	147060.	1.13	1.10	
16	93	11×10 ⁻⁶ acid.....	.189	6.94	1.465	1.42	
	95	Neutral.....	.189	6.94	1.465	1.42	
18	93	211×10 ⁻⁶ acid.....	.207	5.20	1.204	1.24	
	95	Neutral.....	.207	5.20	1.204	1.16	
18	93	211×10 ⁻⁶ acid.....	.050	19.81	1.107	1.15	
	95	Neutral.....	.050	19.81	1.107	1.10	
19	95do.....	.040	24.80	1.11	1.33	Cup hydrogenated for 4 hours
	93do.....	.040	24.80	1.11	0.91	Cup oxygenated for 4 hours
19	95do.....	.040	24.81	1.11	1.02	Immediately following the preceding. No further treatment of the cups
	93do.....	.040	24.81	1.11	1.03	
20	95do.....	.040	24.89	1.113	1.20	Cup hydrogenated for 4 hours
	93do.....	.040	24.89	1.113	0.93	Cup oxygenated for 4 hours
20	95do.....	.040	24.55	1.098	1.05	Immediately following the preceding. No further treatment of the cups
	93do.....	.040	24.55	1.098	1.03	

E. INFLUENCE OF SEPTA OTHER THAN FILTER PAPER**1. SILK**

The influence of silk upon the weight of silver deposit has been discussed in the first paper. The explanation of this effect will be briefly considered here.

Ordinary raw-silk cloth purchased in the open market, part of which has been used as septa in voltameter work, was extracted with pure neutral double distilled water. The extract was distinctly basic toward iodeosine (in ether-water solution). The extract from approximately five grams of the silk was distilled and the distillate tested for furfuraldehyde by means of the very sensitive xyloidine test described in the second paper of this series. No reaction for this aldehyde was obtained. However, the distillate restored the color to magenta solution which had been decolorized with sulphurous acid, thus indicating the presence of an aldehyde of some kind. No attempt was made to identify the particular aldehyde (or aldehydes) formed.

Examination of these aqueous extracts of silk (after careful filtration through asbestos and finely divided platinum) by means of the ultra microscope, showed them to be distinctly colloidal in character.

It is thus apparent that the chemical and physical properties of aqueous extracts of raw silk (unwashed) are very similar in these important respects to the aqueous extracts of filter paper except as to the particular kind of aldehyde formed by its decomposition, so that their very similar influence in the voltameter is probably due to the same causes, viz, the production of permanent colloidal solutions of metallic silver. Indeed such silver hydrosols have been formed and they are very similar in appearance to those prepared from filter paper.²³

The effect of thoroughly washed silk, or more especially of silk which has been used repeatedly in the voltameter is somewhat different. In this case the silk is not decomposed into aldehydes (which probably come from the so-called silk glue) but may be hydrolysed, perhaps, into amino acids thus rendering the electrolyte acid and in consequence decreasing the weight of the silver deposit. Some experiments on this decomposition are given in International Report, page 179.

²³ The influence of gelatine is probably due to the same cause.

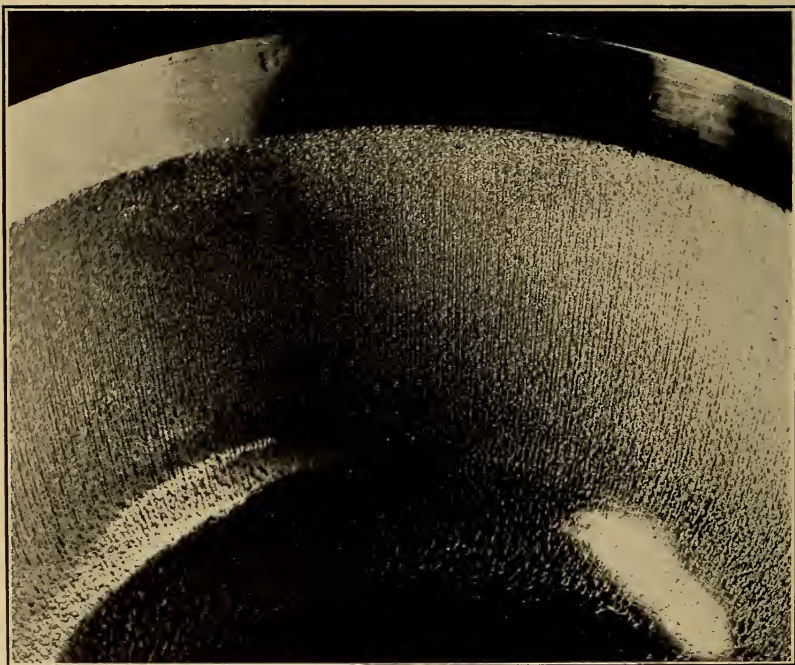


Fig. 5.—*Showing striations due to silk*

The above discussion of the action of silk on the electrolyte was written before we read Von Steinwehr's recent article,²⁴ in which he denies this effect. We have stated that the initial effect of silk in the voltameter is analogous to filter paper and have presented chemical evidence to prove it. To supplement this we publish here a photograph (Fig. 5) of a striated deposit (made while the International Committee was working in Washington) resulting from the use of pure raw silk.

This is a photograph of deposit No. 69 in the tenth experiment made by the International Committee May 2, 1910. The pure raw silk used had been thoroughly washed, but had been kept dry for about two months and was washed again just before the experiment. The value for the cell computed from this deposit was 1.01855, which is abnormally high, being 28 in 100 000, above the mean value. A piece of the same silk was wrapped around a porous cup in deposit No. 71 of the same experiment and increased the deposit over its mate No. 70 by 32 parts in 100 000. This seems to us conclusive evidence that silk is a dangerous substance to use in the voltameter.

As to the second effect of silk, whereby acid is produced, we wish to clearly state that this effect does not influence the result simultaneously with the effect mentioned above. It appears only after the prolonged use of the silk has removed the soluble so-called "silk glue," which gives rise to the effects analogous to filter paper. Table LV of the International Report shows that two samples of silk used by the German delegate produced on the average 30×10^{-6} parts of acid in 160 cc of electrolyte after shaking all together for 24 hours. We tabulate below all the silk observations made by the German delegate in the experiments conducted by the committee as a whole. We give the absolute value computed for the cell in each case except the last where it is not available. In this case we have assigned the value 1.0183 adopted by the committee to the mean deposits obtained by the English, French, and American delegates and on this basis have computed values for the German cups. In column Δ we give the differences between the mean values and the 1.0183 value adopted by the committee.

²⁴ Zs. f. Instr., 83, p. 321; 1913.

TABLE 12
Showing Effect of Silk on Voltameter Deposits

Date	Value	Mean	Δ
1910			
Apr. 15.....	1.01830 ₄	1.01830 ₄	$\times 10^{-5}$ + 0 ₄
20.....	827 ₅		
	837 ₈	832 ₆	+ 2 ₆
26.....	823 ₆		
	820 ₉	822 ₂	- 7 ₈
May 2 ²⁵			
7.....	824 ₆	824 ₆	- 5 ₄
14.....	1.01806		
	1.01773	1.01789	-41 ₀

²⁵ Mixed loose silver from filter paper and silk voltameters so that value for silk is not available.

It will be observed that the concordance of the results given by the German delegate with the results obtained by the other delegates as shown by his Tables LVI, LVII, and LVIII in the Report to the International Committee is due partly to the values obtained with voltameters which had no silk. They did not include the observations of May 14 since no absolute values could be computed for these.

Examining the table we have given above we see that his silk voltameters were in agreement with the adopted value at the start or even slightly above, but that the values decreased until at the end most abnormally low values were found.

In spite of all this Von Steinwehr calls the Kohlrausch form of voltameter one free from all trouble and with the highest claim to be a satisfactory instrument.

2. POROUS POTS

We began to make observations on the possible effects of the porous pot upon silver nitrate as early as September, 1909. These tests included the question of the solubility of the materials of the pot in water, the methods of removing from the pores the acid and other chemicals used in cleaning the pots, the cause of the darkening of the pots after long use, their effectiveness as filters, and several other minor questions. As a result of these tests we adopted a standard method for cleaning and preparing the pots

for use in the voltameter, and this method was described in an earlier paper of this series. Unless otherwise stated, all the pots were those made by the Königlich Porzellan Manufaktur. The results of these investigations (made between September, 1909, and February, 1910), on which this method of treatment was based, may be summarized as follows:

The best "conductivity water" (specific conductivity 1×10^{-6}) dissolves a very slight amount of electrolytes from new unused and untreated porous pots when the water is allowed to slowly filter through the pores, the first few cc of such a filtrate showing a specific conductivity varying from 2 or 3×10^{-6} to about 10×10^{-6} or even greater. Such filtrates also show a basicity toward iodeosine varying from 2 or 3 parts in 1 000 000 to a few parts in a hundred thousand (in terms of NaOH).

Repeated washing of new unused pots reduces this "solubility" of the pot to a point where the change in the specific conductivity of pure water produced by filtering the water through the pores is less than 1×10^{-6} , but this requires a great number of washings and is not a practical method of rendering the pots insoluble.

The pots are most easily rendered insoluble (as shown by conductivity measurements and neutrality tests with iodeosine upon the water filtrates) by filtering dilute nitric acid through them and subsequently washing out the acid by filtering successive portions of twice distilled water through them until neither the conductivity nor the neutrality of the water is appreciably affected by the filtration; that is, the specific conductivity of the water must not be changed by more than 1×10^{-6} and the basicity (or acidity) by more than 1 part in 10^6 (in terms of HNO_3). The pots can easily be gotten into this very insoluble condition by one treatment with acid and four or five washings with water. When the pots are heated to redness or above in an electric oven (to remove silver stains or other impurities from the surface and from the pores) they are much more alkaline (after cooling), i. e., the first portions of water filtered through them are strongly alkaline. This is due to the partial volatilization of the combined alkalis of the silicates of which the pots are composed, the free alkali condensing in the pores and on the surface as the pot cools. This free alkali may be quite easily removed by allowing one or two

portions of dilute nitric acid to filter through. When this acid is removed with the water as before, the pot is again in a highly insoluble condition.

When a 10 per cent solution of pure silver nitrate is filtered through a clean porous pot which has been rendered insoluble and neutral in the manner described above, the filtrate of silver nitrate solution is slightly acid, the maximum amount of acid which we have observed in the first 10 cc of filtrate was approximately 1 part in 10^5 . This acidity decreases as successive portions of the silver nitrate solution are filtered through the pot. If the pots be entirely filled each time with the solution and the whole of the solution be allowed to filter through, the second filtrate shows less than one part in a million of acid. If now distilled water be filtered through the pores until the filtrate is again neutral and free from silver nitrate and the pot be allowed to dry, it again possesses the property of bringing about the formation of traces of acid in the first portions of silver nitrate solution filtered through it. This seems to indicate that the reaction (whatever its nature) whereby acid is produced is at most only very slight and very soon reaches a condition of equilibrium, but that when the products are completely removed this condition of equilibrium is disturbed and the reaction can repeat itself.

For the foregoing reasons the recommendation was made to filter at least three portions of electrolyte through the porous pots before using them in the voltameter for the first time, and for the same reasons it is not permissible to wash the pores free from silver nitrate after use; indeed, the pots are in their most resistant condition when the pores are kept saturated with the same electrolyte that is to be used in the voltameter. When a porous pot is prepared and kept in accordance with the foregoing specifications it is by far the most resistant porous septum which has yet been used in the voltameter.

With regard to the nature of the action whereby the very slight amount of acid is formed when pure neutral silver nitrate solution is filtered through a clean insoluble porous pot, we devoted considerable effort to the study of this question immediately after the effect was first observed and came to the conclusion (1) that the action was catalytic in nature and (2) that the final result was

a very slight reduction of the AgNO_3 to metallic colloidal silver with the formation of an equivalent amount of nitric acid. The observations which led us to this conclusion may be summarized as follows:

1. The first portions of the filtrate show a very slight reduction of $\frac{N}{1000}$ KMnO_4 solution.²⁶ Since tests showed that nitrites were not present, and since we have shown that colloidal silver reduces KMnO_4 solution it seemed evident that this reduction was due to colloidal metallic silver. The second and third following filtrates show no such reduction (or acidity).

2. Clean insoluble porous pots exercise a reducing action upon at least one other substance besides AgNO_3 , viz, chromic acid. This effect was first observed when cleaning porous pots with the chromic acid mixture. If chromic acid (of normal strength with respect to hydrogen) be allowed to remain in the pores for a day or so and then washed out the solution has a distinctly olive-green color indicating the presence of a chromic salt (i. e., Cr_2O_6 has been reduced to Cr_2O_3). The chromic salt may be precipitated as chromic hydroxide $\text{Cr}(\text{OH})_3$ by ammonia. It was at first thought that this reduction must be due to dust or organic impurities in and on the pot but the effect could be repeated with the same pot after thoroughly washing out the acid until the conductivity of the purest water was unchanged by filtration through the pot and when the pot had been heated to bright redness in the electric furnace and the greatest care taken to subsequently exclude all dust and organic impurities. Furthermore, blank experiments with the same chromic acid in the same surroundings but not in contact with a porous pot gave negative results. Since these results were obtained we have learned that a somewhat similar phenomenon was observed by Tscheishvili²⁷ with solutions of potassium permanganate and asbestos filters. It is not shown, however, that this effect is due to a reducing action on the solution.

²⁶ This effect of porous siliceous material upon silver nitrate solution is discussed by H. E. Patten (J. Phys. Chem., 14, p. 612, 1910). This phenomenon and also the production of acid by the action of porous pots upon silver nitrate solution had been observed in this laboratory and the results had been discussed in a conversation between one of the present authors and Dr. Patten before the publication of the latter's article.

²⁷ J. Russ. Phys. Chem. Soc., 42, p. 856, 1910.

3. Other explanations of the formation of acid by the filtration of silver nitrate solutions through the pores are not in agreement with the facts, as, for example, the possibility of a double decomposition of the silicates of the pot by interaction with AgNO_3 resulting in the formation of strongly hydrolysed (and therefore acid) salts of the bases of the silicates (e. g., MgO , Al_2O_3 , etc.), for such an action would not account for the presence of reducing substances in the filtrate. Likewise the possibility that colloidal AgOH is filtered out by the process, the hydroxide remaining behind on the inner wall of the pot is untenable, for this also would not account for the formation of reducing substances. Such an action as the above is known to take place with solutions of ferric salts.

The mechanism by which this catalytic reduction of AgNO_3 (and chromic acid) is brought about is a matter of conjecture, but this does not alter the facts in the least. Whether the reduction is brought about by the direct discharge of positive silver ions upon the negative walls of the pores or by the formation of some intermediate product (such as peroxides) which subsequently decompose, giving rise to the same end products can not be determined from the known facts.

3. ELECTROSTENOLYSIS

The foregoing phenomena offer a satisfactory explanation of possible electrostenolysis in the porous pot, i. e., deposition of metal by the current at points other than the primary electrode. The function of the porous septum seems merely to be that of any catalytic agent; that is the rate of the spontaneous decomposition of silver nitrate into metallic silver (which under normal conditions is inappreciable) is enormously increased by contact with a porous septum, resulting in the deposition of minute traces of metallic silver in the pores.

After some metallic silver (no matter how small an amount) has been formed in the pores, the stenolytic process proper, i. e., the increase in the amount of silver in the pores by the action of the electric current, is probably due to the silver being deposited on the cathode side of a particle (i. e., the side nearest the anode of the voltameter) at a greater rate than that at which it dissolves from its anode side. This difference in rate is proba-

bly due to the formation of silver peroxynitrate ($\text{Ag}_7\text{NO}_{11}$) or some other product which tends to render this side of the silver particle "passive."

This stenolytic action is, of course, dependent upon the current density through the pores, the potential gradient, and the percentage strength of the electrolyte. This action can at most be but very slight under working conditions; indeed, there is no experimental evidence that it occurs at all under the normal conditions in the voltameter, since the very slight amount of acid formed in the cathode chamber may be produced by the porous pot when no current is flowing. Moreover, the factors which cause electrostenolysis proper are identical with those which cause secondary reactions at the anode of the voltameter under normal conditions (i. e., high current density and dilute electrolyte). Therefore abnormal conditions of concentration and potential gradient which favor stenolysis would also affect the electrolyte around the anode in any nonseptum form and in exactly the same manner. It would seem, therefore, that any conclusions as to the possible evil influence of the porous pots under normal conditions deduced from the effects produced under the exaggerated conditions necessary for the production of stenolysis would apply as well to one case as to the other, so that in this respect no advantage can be argued for the use of a nonseptum form of voltameter. The disadvantages of nonseptum forms due to anode slime have been sufficiently explained.

Richards has shown that even in very exaggerated cases of electrostenolysis the weight of silver deposited is not appreciably affected. F. E. Smith has obtained lower values when the conditions were selected so as to produce pronounced stenolysis in the porous pots,²⁸ but entirely similar results would doubtless follow if the same conditions of dilution and fall of potential were purposely produced at the anode itself, so that this evidence does not condemn the porous pot. The only legitimate objection which can be urged against the porous pot is that it does produce a very slight catalytic action upon the electrolyte independently of the action of the current; but with porous pots prepared in accordance with the specifications given, this action is too slight to influence

²⁸ Private communication.

the weight of the deposit, as the results of the numerous experiments with the porous-pot voltameter show. On the other hand, if no septum whatever is used the difficulty of dealing with the anode slime and the possibility of the formation of base at the anode are quite as serious objections as those suggested above concerning the porous pots. Actual comparisons have shown that both of these possible sources of error are easily controlled in actual practice.

F. PURITY OF THE SILVER DEPOSIT

1. CONSTANCY OF ANY ERROR DUE TO INCLUSIONS

The possibility of the inclusion of foreign material in the silver deposits has been recognized since the time of Lord Rayleigh's work in 1884. Many attempts have been made to measure the quantity of such inclusions as well as to determine their nature. The results of different observers are contradictory. The work of the present authors has demonstrated that under proper conditions the average deviation of a single observation from the mean of a series can be made as small as a few parts in one hundred thousand.

TABLE 13

[Size of voltameter, large, medium, and small, are indicated by the letters lms]

Observations	No.	Voltameter	Mean value for cell	Average deviation of a single determination
First series.....	42	Porous pot (lms).....	1. 01828 ₇	6 in 100 000
Second series.....	44	Porous pot (s).....	1. 01827 ₅	3 in 100 000
Second series.....	18	Porous pot (lm).....	1. 01832	4 in 100 000
Third series.....	156	Porous pot (lms).....	1. 01826 ₇	3 in 100 000
Third series.....	55	Smith form (lms).....	1. 01827 ₄	4 in 100 000

The uniformity of the means as well as the smallness of the average deviations show that either there are no significant inclusions of liquid or other foreign matter in the crystals or else that such inclusions are very constant in amount. The deviations shown in the above table include many sources of error beside the inclusion in the crystals, such as errors in timing the deposit, the constancy of the current, washing and drying the deposit, besides the errors of weighing the bowls both with and without the silver deposit. It is not likely that in a silver crystal formed perfectly

according to the cubic system or one of its modifications that any appreciable amount of inclusions would be possible. Colloidal particles, however, form nuclei for new crystals, and it seems plausible that the inclusions if present are caught between the crystals as they form. This would not happen often, however, in the case of pure electrolytes which contain very little colloidal matter. It is not necessary that we should know what the amount of the inclusions is so far as the measurement of the international ampere is concerned, since the defined electrochemical equivalent, 1.11800 mg per coulomb, is for the silver as we find it deposited in actual practice in the voltameter. But it is important, if possible, to eliminate any error due to the inclusions from an absolute determination of the electrochemical equivalent in order to compute the value of the faraday.

2. PREVIOUS DETERMINATIONS OF INCLUSIONS

Lord Rayleigh and Mrs. Sedgwick²⁹ made two attempts to measure the inclusions in their deposits. In the first place they dissolved deposits in HNO_3 and precipitated the silver with NaCl , comparing the results with pure silver obtained from Johnson and Matthey, but the results were inconclusive. They then tried heating the deposits to incipient redness, finding a loss of about 0.010 per cent in the deposits made from AgNO_3 and 0.1 per cent in the deposits made from AgNO_3 electrolytes to which acetate had been added. The results of our own work would lead us to expect in the former case an even greater loss than they found, since they were using the filter-paper voltameter. This is because the silver colloid formed by the action of the filter paper on the electrolyte tends to break up the crystalline structure of the silver as we have shown elsewhere³⁰, permitting greater amounts of the liquid to be included, besides organic matter from the paper itself. The smallness of their result may be readily explained by the assumption that they did not drive out all the foreign material. In case of the acetate the large loss is not surprising, since the presence of the acetate causes a very complete destruction of the ordinary silver crystals, and consequently much larger quantities of foreign material may be included.

²⁹ Phil. Trans., 175, p. 411.

³⁰ This Bulletin, 9, p. 263.

Thomas Gray ³¹ on the other hand noted that deposits properly washed may be heated in a spirit flame without loss in weight.

Richards, Collins, and Heimrod ³² made an analysis of their deposits by dissolving the silver of a filter-paper voltameter in HNO_3 and precipitating with HBr . They found the mean deficit of silver to be 0.007 per cent, but by correcting apparent numerical errors in Nos. 35 and 36 of their table this is reduced to 0.002₅ per cent. Later Richards and Heimrod ³³ redetermined the inclusions in the silver by heating the deposit to incipient redness. They give as the mean loss in weight 0.018 per cent, but note that it varies somewhat with the conditions of the experiment.

Van Dijk ³⁴ heated the platinum crucibles with their deposits in an electric furnace. His conclusion was that the deposits, as ordinarily made, contain no appreciable inclusions, but if a deposit is made upon another deposit which has been heated to redness a considerable loss in weight is observed the first time the new deposit is heated. This he ascribed to fissures and cavities in the old deposit caused by the strains created when it was first heated to a high temperature. These cavities inclose liquid when the second deposit is made and they are sealed off by the new silver. Since 500° is sufficient to expel this liquid the first time the cup is heated, no further loss being detected on subsequent heatings, he concluded that none of the deposits can contain inclusions after being thus heated. In some cases he used a temperature as high as 600°. His experiments were chiefly on deposits made in the porous-cup voltameter.

Smith, Mather, and Lowry ³⁵ tried heating a few deposits over a Bunsen flame and found no loss. They then accepted Van Dijk's results without question.

Jaeger and Von Steinwehr ³⁶ heated a number of the deposits in the crucibles over a Bunsen flame; they found small losses which, however, were not as great as the crucibles suffered when empty. They therefore concluded that the inclusions are insignificant.

Duschak and Hulett ³⁷ again took the matter up because of the contradictory results of Van Dijk and of Richards and Heimrod.

³¹ Phil. Mag., 22, p. 399; 1886.

³² Proc. Am. Acad., 35, p. 138; 1899.

³³ Zs. f. Phys. Chem., 41, p. 321.

³⁴ Arch. Neer. des Sci. II, 10, p. 277; Ann. der Phys., 19, p. 246.

³⁵ Phil. Trans., 207, p. 579.

³⁶ Zs. f. Instr., 12, p. 354.

³⁷ Trans. Am. Electro Chem. Soc., 12, p. 257.

They placed a definite quantity of deposit in combustion tubing connected to a small manometer and sealed it off after drying the interior of the apparatus and evacuating it. When the heating of the deposit began an increase in the pressure was noted that progressed in stages as successively higher temperatures were reached until the maximum of about 600° was reached. In one experiment using a quartz bulb the temperature was carried up to the fusion point of silver, but the gas liberated after passing 600° was very small in amount. They condensed the water vapor in a capillary tube so that this could be distinguished from the other gases. They concluded that the total inclusions on the average were about 0.011 per cent, and that they were distributed throughout the crystals. In the case of deposits made in vacuo the inclusions seemed somewhat less.

The subject was again taken up in a paper by Laird and Hulett.³⁸ They made some modifications of the preceding method of which the most important was to alloy the silver with tin in order to reduce the temperature required for complete expulsion of the inclusions. They also endeavored to identify the substances given out, and from the amount of nitrogen found, to compute the amount of entrapped silver nitrate; but this method suffers from the disadvantage that errors necessarily present in so difficult a determination are multiplied by 12, since $N:AgNO_3::1:12$. Their main conclusion was that silver nitrate in appreciable quantities is present in the silver crystals, but probably does not exceed five parts in 100 000 for the best deposits.

3. EXPERIMENTS ON INCLUSIONS At the Bureau of Standards

(a) *Detection of Silver Nitrate.*—For the estimation of the included silver nitrate the deposit after being carefully removed from the platinum cup was alloyed with fifty times its mass of pure redistilled mercury and the alloy then shaken up with double distilled water. Any silver nitrate present would be liberated by the alloying process and would dissolve in the water. We thought that even very small amounts could be detected by means of phenol sulphonic acid in the usual manner for estimating small amounts of nitrates. Some difficulty, however, was encountered

³⁸ Trans. Am. Electrochem. Soc., 22, p. 345.

in detecting in this way the small amounts of silver nitrate purposely added to silver amalgams to test the method. It was thought that the trouble was due to the presence either of silver or mercury salts or to both in the solution. Mercury displaces silver to a limited extent from aqueous solutions, a condition of equilibrium being reached in which both silver and mercury are present in the solution. Any mercury salts present in the solution must be in the mercurous condition because of the excess of metallic mercury present. Therefore to completely remove both silver and mercury from the solution it is only necessary to add a few drops of hydrochloric acid. This changes the nitrate present into nitric acid, in which form it can be readily estimated colorimetrically by the phenol sulphonic acid. Blank tests showed that quantities of silver nitrate corresponding to less than one part in one hundred thousand of the silver present in the amalgam could be easily detected and larger amounts could be estimated.

Several normal silver deposits were examined by this method for occluded silver nitrate, but only the faintest traces (less than 0.001 per cent) were found. It is therefore certain that any error due to included silver nitrate alone is entirely negligible in the case of our normal deposits from the purest electrolyte. It remained to be shown, however, whether this was also true for the abnormally heavy deposits from contaminated electrolyte, as, for example, the deposits from the filter-paper voltameter. Accordingly several of these were also examined in the same way, with the result that a very small but definitely larger amount of nitrates was found. In making the estimation, the color produced was matched with that formed by the addition of a known amount of standard silver nitrate solution to a thoroughly washed amalgam, all of the conditions as to dilution, temperature, etc., being exactly the same in the two cases. The amounts of nitrate found in the silver deposits obtained from the filter-paper voltameter varied from one to two parts in one hundred thousand. The error due to the inclusion of silver nitrate alone can not, therefore, be greater than one or two parts per hundred thousand even in deposits which are heavier than the normal deposit by as much as ten to forty times this amount.

(b) *Estimation of Included Water and Volatile Material.*—It appeared from the foregoing results, therefore, that if the excess (Δ) in mass of the deposits from the filter-paper voltameter over those from the Richards type is due to inclusions (of some kind), they must consist of some impurity other than silver nitrate itself. Water seemed the most probable single inclusion other than colloidal silver which could be present in amounts sufficient to account for the greater portion of this excess; for the electrolyte immediately next the cathode where the silver is being deposited must necessarily be much more dilute than the average concentration of the whole electrolyte. It seems highly probable that the inclusions (if present at all) must have practically the same concentration as this depleted electrolyte. This would mean that the deposit from an electrolyte of an average concentration of 8 per cent (such as may be present in the cathode chamber of the small size Richards voltameters) would consist of not less than 92 per cent water, the more probable value being something like 95 to 98 per cent or even greater.

Accordingly experiments were planned to determine with the greatest possible accuracy the total amount of water included. The indirect method of noting the loss in weight of the silver crystals when they are alloyed with some nonvolatile metal was finally decided upon as the most practical way of accomplishing this result.

A careful consideration of all the nonvolatile metals which might be used for this purpose led to the selection of platinum as the most suitable. Accordingly, arrangements were made to alloy the silver deposit with the platinum crucible in which it was originally deposited, making very careful weighings to determine any loss in weight.

The heating was done by means of a good alcohol flame, and the change in weight of the crucible alone (heated in the same manner as when alloying the silver) was carefully determined before the silver was deposited in it. Likewise after alloying the silver, the crucible was again heated to determine whether the weight had become constant. The question of the volatility of the silver under the conditions could thus be accurately checked.

To facilitate turning the crucible while in the flame in order to completely alloy every portion of the silver, a handle of stiff platinum wire was fused to the crucible so that it could be readily handled with platinum-tipped tongs. A tightly fitting platinum cover for the crucible was kept in place during the heating and only one part of the crucible was heated at a time, so that there was always a large cool surface to condense any silver vapors which might volatilize.

The time available for this part of the work permitted the carrying out of only a single determination, the results of which are given below. The deposit alloyed was from electrolyte strongly contaminated with filter paper. This was purposely chosen for this first experiment because it was thought the loss in weight would probably be larger than from a normal deposit. Also it should throw some light on the question as to whether the excess mass is due mostly to occlusions or to colloidal silver itself. In the event that the former case proved true, our first conclusion that the principal rôle of the colloid is in breaking up the crystalline structure of the silver deposit, so that more electrolyte is included, would be confirmed.

Platinum cup empty:	mg
Loss of weight after first heating (10 min.).....	0.075
Loss of weight after second heating (10 min.).....	0.001
Loss of weight after third heating (10 min.).....	0.009

Loss after first heating was probably due to some volatile material on the surface of cup before being used.

Platinum cup with silver:	mg
Weight of silver deposit.....	1093.920
Excess weight over pure deposit.....	0.560
Loss after alloying with platinum.....	0.536
Change (gain) after second heating.....	0.030

The process of amalgamation consumed more time than we had anticipated, hence we again heated the cup as before for about the same time (one hour), but found only a very small change.

The almost exact equality between the loss in weight upon alloying and the excess weight (Δ) of the deposit over the normal deposit would seem to indicate that the inclusions in the normal deposit are negligible.

(c) *Estimation of Organic Material.*—We have already discussed this in Part II of this series of papers. (See Vol. 9, p. 241.) Any

of this material would of course be consumed in the alloying process given above for determining the presence of water.

(d) *Titration of the Silver Deposits.*—The ease with which we succeeded in making the silver estimations of small deposits when studying the acid effect led us to try to extend the method to titrate larger deposits. We hoped that by standardizing our ammonium sulphocyanate solution against some of our best electrolytic silver we might successfully measure the difference in silver content of a pure and an impure deposit. The indicator was prepared according to the method of Hoitsema.³⁹ We did not succeed as well as we had hoped, however, since the end point was transient when the samples of silver were more than one or two-tenths of a gram. We therefore were obliged to abandon the effort.

(e) *Conclusion.*—We do not regard the matter of inclusions in the silver deposits as satisfactorily settled. We believe that in the best deposits they are very small, probably less than 5 parts in 100 000, as estimated by Hulett. Our determinations of the silver nitrate present in the crystals are unfortunately directly opposed to his, so that for lack of further evidence we can not decide this point. The work of one of the present authors (Vinal) jointly with Dr. Bates, of the University of Illinois, on a comparison of the silver and iodine voltameters for the measurement of the faraday emphasizes the desirability of investigating the inclusions further. The value for the faraday is computed and discussed in their paper.⁴⁰

G. REVERSIBILITY OF THE SILVER VOLTAMETER

In some of the earliest researches on the silver voltameter the current was measured by the loss in weight of the anode as well as the gain in weight of the cathode. This was true of Mascart's and Gray's work, but the differences tolerated in those days were greater than is considered permissible to-day. If Faraday's laws of electrolysis hold strictly for the silver voltameter there should be an equivalence between the loss of silver at the anode and the gain at the cathode, but with the advent of the complex ion theory no further efforts were made to measure quantitatively the changes

³⁹ Zs. f. Anorg. Chem., 17, p. 647; 1904.

⁴⁰ This Bulletin, 10, p. 425; 1914 (Reprint No. 218).

taking place at the anode. Washburn and Bates⁴¹ reflect the current opinion when they say "The reaction in the silver coulometer is not reversible."

Since our work has shown that the complex ion heretofore ascribed to secondary reactions at the anode is probably non-existent and that the effects supposedly produced by it are due to colloidal particles either present in the electrolyte or produced by substances (such as filter paper) introduced into the electrolyte, it seemed worth while to investigate further the question of reversibility.

Before making any quantitative experiments we began by considering the acid and potential changes taking place in the voltameter during the progress of an experiment. For this purpose it was most convenient to use as an anode the silver coating on the inside of a platinum bowl the electrolyte in which was connected through a siphon with that in a second bowl serving as cathode. This facilitated taking samples of the anode and cathode liquids for acidity tests and also measuring the potential changes between the bowls and some reference points which were fixed at the end of the siphon. With such an anode the liquid was in contact with both silver and platinum as in the case of the cathode. In the latter we know that after the deposit begins the current flows solely to the silver crystals, so that the question at once arose whether the current passing from the anode solution would do so from the silver crystals alone. This was found to be true provided that the amount of silver was not too small. It was easily proved by the absence of silver peroxynitrate crystals and by the absence of an increase in acidity of the anode liquid almost to the end.

Samples of the electrolyte for acidity tests were taken at stated intervals and the potential differences were measured on a high resistance potentiometer between the platinum cups and the ends of the siphons where fine silver wires dipping into the electrolyte were fastened. The results of these experiments are best shown graphically, and in the accompanying curves (Figs. 6 and 7) we give the acidities and potentials plotted as ordinates against the amount of silver remaining on the anode bowl as

⁴¹ J. Am. Chem. Soc., **34**, p. 64; 1912.

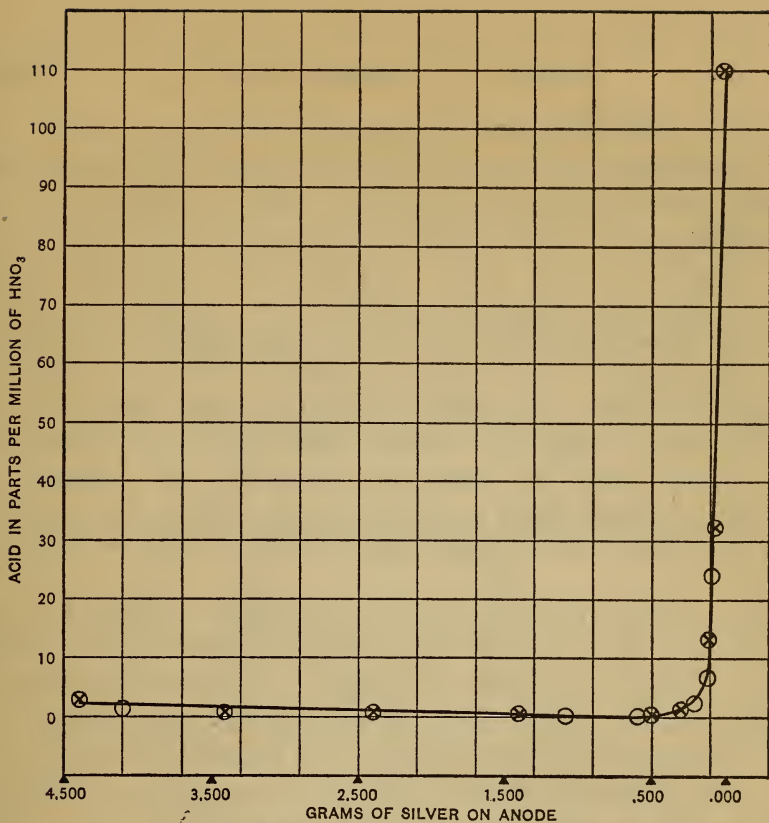


Fig. 6.—Changes in acidity of anode liquid

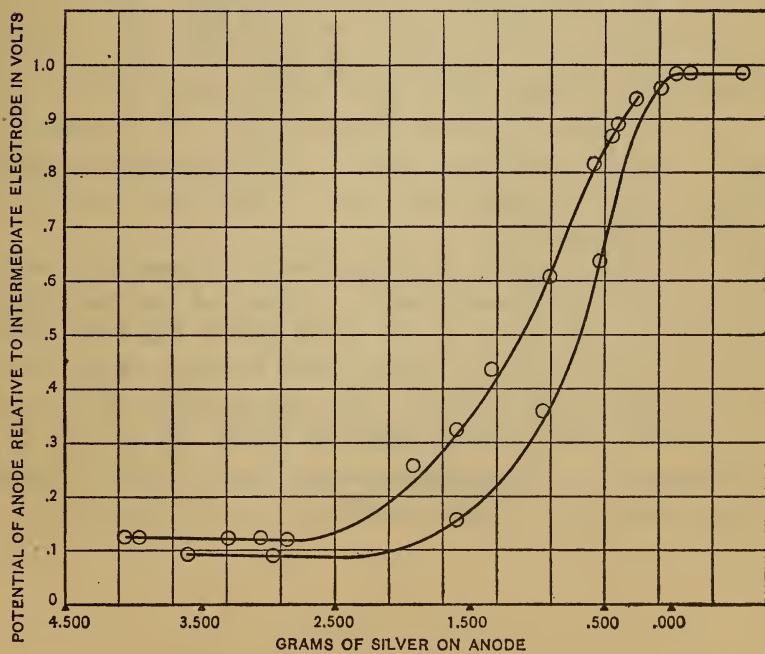


Fig. 7.—Changes in potential of anode

abscissa. This is of course a function of time and current. In the experiments we have kept the current as constant as possible under the circumstances so that we might compute the silver remaining on the anode from the time of taking the observations. The abscissa marked "0.00" represents the theoretical exhaustion of silver according to the equation $M = 1.11800it$, M being the mass of silver taken off the anode in milligrams and i the current in amperes and t the time in seconds. This is not, however, strictly true, since the secondary reactions begin when the break in the curve comes. This means that current is passing into the solution from the platinum surface with the formation of $\text{Ag}_7\text{NO}_{11}$ crystals which speedily become visible. Consequently at the abscissa "0.00" some silver is still to be seen on the anode bowl.

Fig. 6 shows the results of two experiments (indicated by the crosses and circles, respectively), made to determine the relation of the acidity of the anode electrolyte to the amount of silver remaining on the anode. The crosses represent observations when the current was one-fourth ampere and the circles when the current was one-third ampere, but there is no difference between them. Fig. 7 gives the curves for the potential of the anode relative to an intermediate electrode. For the left-hand curve the current was one-half ampere and for the other one-third ampere. The anode was always positive with respect to the intermediate electrode. The slight initial decrease in potential was due to the small increase in temperature of the electrolyte before a steady state was reached. The maximum potential difference occurs at about the time of theoretical exhaustion of the silver on the anode.

Fig. 8 gives the complete data regarding both anode and cathode changes of one experiment using a current of one-half ampere. One doubtful observation on the anode acidity has been omitted as there is some reason to believe that it was confused with a sample taken from the cathode. The characteristics of the acidity and potential curves for the anode are about the same as in the preceding curves. The cathode curves II and IV show relatively uniform conditions to hold throughout the experiment.

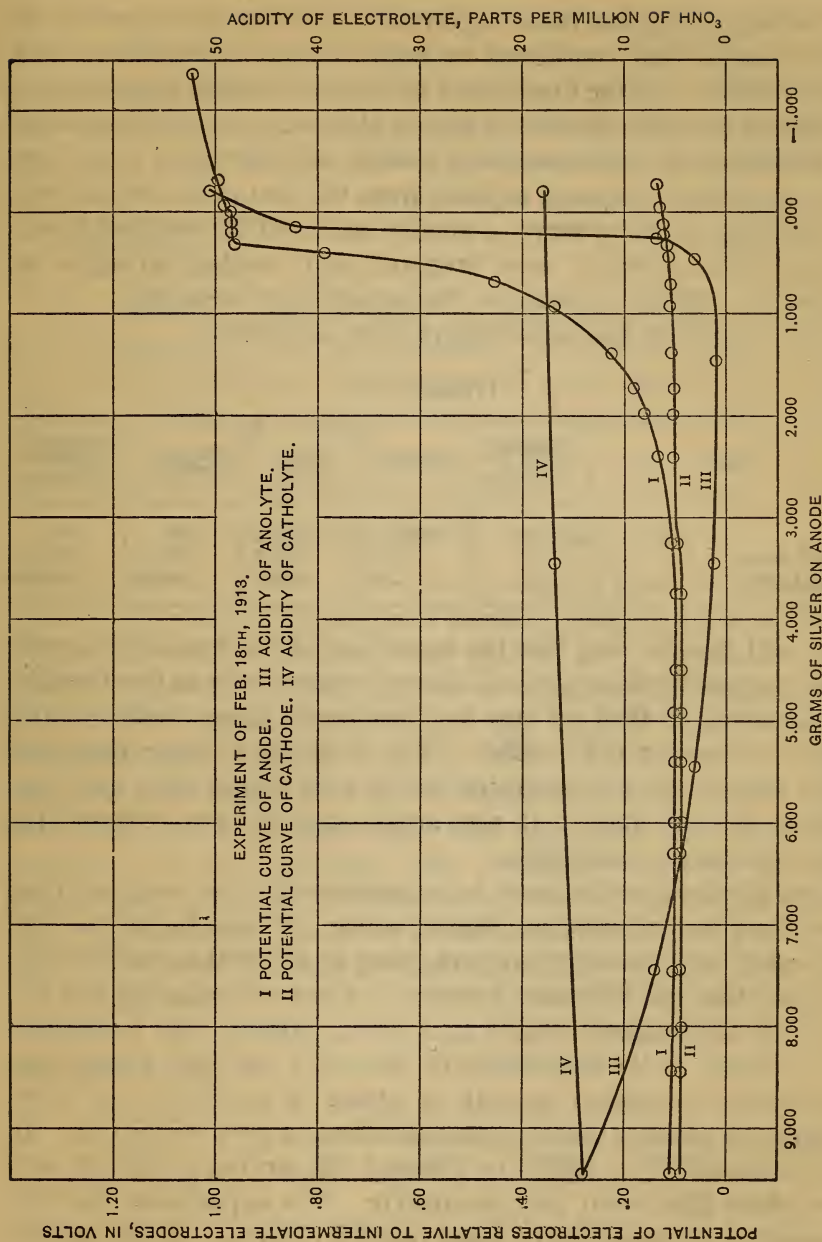


Fig. 8.—Acidity and potential curves for both anode and cathode

Having completed these experiments we were in a position to know under what conditions we might expect the voltameter to be reversible. In the first place a large anode surface was desirable to reduce the slime, and in the second place we saw that the amount of the silver on the anode bowl should not fall below 2.5 or 3 g. We accordingly prepared deposits from the best electrolyte in two of the large bowls to serve as anodes and carefully weighed them. Other bowls (empty) were prepared and weighed to serve as cathodes. Siphons connected the anodes and cathodes.

The results of two experiments were as follows:

TABLE 14

Date	Weight of silver on anode bowl	Current	Loss at anode	Gain at cathode	Deposit in standard Smith form
	g	amp	mg	mg	mg
Feb. 27, 1913.....	8	0.500	2164.81	2164.78	2164.81
Mar. 11, 1913.....	9	.500	2092.12	2091.92	2091.83

It will thus be seen that the agreement of the loss at the anode with the gain at the cathode is about the same order as for standard voltameters, so that we may say that under these conditions the silver voltameter is reversible. This indicates a nearer approach to a simple reaction according to Faraday's laws than has been before thought likely. It also argues that for pure electrolytes the inclusions are negligible.

One further question arose in connection with this work and that was the effect of using an impure anode. It was hoped that by reversing the voltameter as above, using an anode that was strongly striated that the difference between the loss at the anode and the gain at the cathode might give some data on the inclusions. Accordingly, in the experiment of March 11 we used a large cup containing a striated deposit of about 9 g, which was more than 8 mg excess over its mate made from a pure electrolyte. It was connected by a siphon to a second cup serving as cathode and the whole filled with pure electrolyte. The experiment had not proceeded far before there was a marked difference in the appearance of the anode bowls. That containing the pure deposit remained white and at the end contained little anode slime while

the other turned dark and at the end contained an abundance of fine brownish slime that made great trouble in washing the bowl, as we have already described on page 500. All this slime which could possibly be recovered was put back in the bowl. After washing it was dried and weighed. The results were as follows:

	mg
Anode lost.....	2095. 43
Cathode gained.....	2092. 21
Standard Smith form.....	2091. 83

The conclusion leaves no room for doubt that the purity of the anode is essential in such an experiment. The excess of its cathode over the standard form, which from the other cathode appears a little low (Table 14), suggests that such impurities as were contained in this anode may influence the deposit on the cathode, as we have already suggested more at length on page 500.

H. A SIMPLE VOLTAMETER OF SMALL COST

It seemed worth while to design if possible a form of voltameter which would give a fair degree of accuracy, but at the same time be an inexpensive instrument for general use. The anode was made in the form of a large ring set in a glass dish containing the electrolyte. This silver ring was made large to minimize the difficulties with the anode slime. The cathode was a small platinum ring resting in a shallow glass dish submerged in the electrolyte and so arranged that the whole might be lifted out together. As this platinum ring weighed only 10.5 g, the largest item of expense was reduced to about one-tenth that of the large size standards. It is not intended that this form should be used in any work requiring the highest precision, but the following comparisons show that it may be relied on to a few hundredths of 1 per cent. The arrangement of the parts is shown in the accompanying drawing (Fig. 9):

Date	Approximate time	Approximate current	Deposit in standard	Deposit on the ring	Difference
July 29, 1912.....	sec 3615	amp 0. 510	g 2. 04734	g 2. 04748	—7 100 000
Aug. 1, 1912.....	3615	. 510	2. 04879	2. 04860	+9 100 000

IV. VOLUME EFFECT

In our third paper⁴² we have described a phenomenon which we have designated as the "volume effect." This is manifested in the case of impure electrolytes by an increased weight of deposit in the large bowls over that in the small bowls, used simultaneously, the excess of the former being roughly proportional to the difference

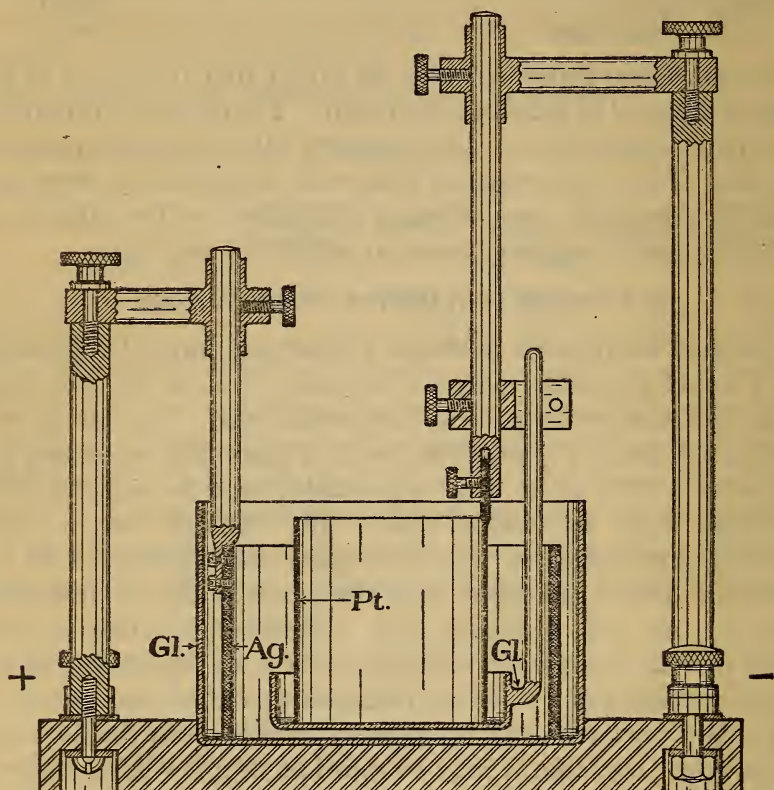


Fig. 9.—A voltmeter of small cost

in volume of the cathode liquids in the two sizes. By learning how to purify the electrolyte we overcame the difficulty. As the results given in this paper show, the large and small sizes agree when the electrolyte is pure. We regard this volume effect as a valuable test of the purity of the electrolyte. We had not intended

⁴² This Bulletin, 9, p. 514 (Reprint No. 201).

to discuss this matter further until specifications are adopted, but a recent paper by von Steinwehr⁴³ seems to call for some further discussion. He says: "We are drawn to the opinion that if the reality of the volume effect may have been established it is, after all, very extraordinary that it has been only observed with the porous-pot type and not to appear in the other types also. It naturally follows from this that this effect is not to be sought in the originally present impurities in the solution, but in the porous pot itself." We have previously discussed this question at some length⁴⁴ and have shown that the volume effect has been observed in other forms of voltameter. We have also given⁴⁵ good experimental evidence that a suitable purification of the electrolyte will eliminate the volume effect.

Going back 30 years, we find evidence of the volume effect in the work of Lord Rayleigh and Mrs. Sedgwick,⁴⁶ who used the filter-paper voltameter. Examining their Table II we find that, averaging all their differences between large and small voltameters for all the observations used for computing the final value, that the deposit in the large cups exceeds that in the small cups by 14.5 in 100 000, and only in one case out of 10 does the deposit in the small cups exceed that in the large cups. We were not the first to recognize this difference since Schuster and Crossley⁴⁷ called attention to it in 1892 and tried to explain it. They say: "A second anomaly lies in a small but regular discrepancy in the deposits when they are taken simultaneously in platinum bowls of different sizes." Their results are given in their Table I (p. 347). In only one observation, which is very discordant with the others, does the deposit in a small bowl exceed that in the large bowl. The mean excess of the large bowls over the small bowls for the other seven observations is 17 parts in 100 000. They say: "* * * the results give a consistent difference of about 2 parts in 10 000 in favor of the large bowl."

The volume effect is also to be observed with the siphon voltameter as pointed out in our third paper.⁴⁸ Indeed, von Steinwehr calls attention to the large values obtained using siphons by Kohl-

⁴³ Zs. f. Instrk., 33, p. 321; 1913.

⁴⁴ This Bulletin, 9, p. 514 (Reprint No. 201).

⁴⁵ This Bulletin, 9, pp. 514-517 (Reprint No. 201).

⁴⁶ Phil. Trans., 175, p. 438; 1884.

⁴⁷ Proc. Royal Soc., 50, p. 344; 1892.

⁴⁸ This Bulletin, 9, p. 516 (Reprint 201).

rausch and Laporte, but in each case he adds that it is due to some hitherto unexplained error! In conformity with these observations our own show the mean value of 10 siphon observations to be 1.01858 volts for the Weston cell at 20°, which is 30 parts in 100 000 over the value as determined by the porous-cup voltameter in the same series of measurements. This difference can not be attributed to experimental error. Moreover we have shown in this paper ⁴⁹ that we have brought the siphon voltameter nearly into agreement with the porous pot and Smith forms by purifying the electrolyte to the highest degree, as we know how to do now. The mean value of five siphon voltameter determinations of the cell given in this last paper is now 1.01832, or 26 parts in 100 000 lower than before obtained, using unpurified electrolyte in the same cups and with the same siphons. Such differences can not be accidental. Further evidence on the volume effect in the siphon form is found on pages 156 and 165 of the Report of the International Technical Committee. The experiment of May 10 included six voltameters of the siphon form, as well as several other standard forms. The electrolytes used were from three sources. That designated as A was prepared by Mr. F. E. Smith of the N P L and was believed to be the purest; that designated as B was as purchased from Poulenc and our tests showed it somewhat impure; that designated as "Old Baker" was found by tests to be the most impure of all. Expressing the results in terms of the mean of all the voltameters taken as unity we find the relative weights, as given in the first part of the table, page 156, as follows:

Electrolyte	Relative weight	Mean
A.....	{ 1.00000 1.00000 }	1.00000
B.....	{ 1.00028 1.00014 }	1.00021
Old Baker.....	{ 1.00023 1.00037 }	1.00030

⁴⁹ This paper, p. 492.

Or compared with the Smith form taken as standard, as on page 157, we find these results as follows:

Electrolyte	Relative weight	Mean
A.....	{ 1.00012 1.00012	{ 1.00012
B.....	{ 1.00026 1.00040	{ 1.00033
Old Baker.....	{ 1.00049 1.00035	{ 1.00042

The obvious conclusion in any case is that the electrolytes gave volume effects in the order of their estimated impurity.

As to the volume effect in the new form no conclusions can be drawn from Table XLVIII, as given by the International Committee, since Mr. Smith did not use an impure electrolyte in a small size of his voltameter, but data is available in Table No. 7 of miscellaneous results given in the present paper. On July 17, 1911, we used an electrolyte as purchased from Baird and Tatlock. This showed a volume effect in both the porous-cup form and the new form, and again on December 14 an electrolyte yielding an abnormal result in the porous-cup form showed a volume effect in the Smith form also. We believe that enough work has been done to show that the volume effect is not confined to the porous-cup form.

Dr. von Steinwehr lays particular stress on three "objection-free" observations contained in Table XLVIII of the report of the International Committee which show small values in large voltameters for electrolyte believed to be impure. But it is impossible to prove that the volume effect is a porous-pot phenomenon from these three "objection-free" observations since two of them were made by Prof. Laporte using Smith's new form of voltameter, as can be seen by reference to the original tables, while the third was made in a porous-cup voltameter by Prof. Laporte using a very small anode, as may be seen by referring to page 148.

We now come to the question of whether the reproducibility of the porous-pot voltameters is sufficient to prove the reality of

the difference between the large and small sizes. Dr. von Steinwehr denies that it is. He points out that the average difference between large and small voltameters in our first series is only 2.5 in 100 000. He would be quite right in saying that we had not proved our point if our evidence rested on this alone. At this time we were using the largest size of porous cup shown in Fig. 2 of our first paper, in the large-size bowls. The bulk of these porous cups so diminished the volume of cathode liquid that its excess over that in the small bowls was not great and hence only a small volume effect would be expected. The volume effect depends of course on the difference in the volumes of the electrolyte in the cathode space, and not on the difference in the sizes of the bowls. We did not discover the volume effect until we began using the smaller porous cups in the large voltameters (second series).

Then we carried the computations back for the first series and found the difference 2.5 in 100 000 recorded above, which, while small, is in the direction to be anticipated. The second series of measurements mentioned by von Steinwehr are of little interest, since all the experiments in which large and small voltameters are compared have been separately tabulated in Table 9 (supplement to report of International Technical Committee), which he calls the third set of observations. In this it is shown that the mean of the large cups exceeds the mean of the small cups by 7 parts in 100 000. However, von Steinwehr does not consider the reproducibility of the voltameter good enough to prove this. If there were no volume effect it would be reasonable to suppose that in half the experiments the deposits in the small voltameters would exceed those in the large sizes, but this is not the case. The deposits in the large voltameters exceed those in the small sizes in every case.

Accidental errors are bound to enter into the observations and hence we must compute a mean result, which is mathematically better than the result of a single observation by the square root of the number of observations. When a difference is observed always in the same direction it can not be called an accidental error. We have shown in Table 7 of the supplement to the international technical committee report that the average reproducibility of the small porous-cup voltameter is $\frac{1}{100\,000}$, or the average

deviations in various runs is 3 in 100 000, yet von Steinwehr comments on the "not very great consistency" of our results when his own results given in Table 5 of his 1908 paper shows his average variation using the Kohlrausch voltameter to be about 9 parts in 100 000 and with the porous-pot form about 8 parts in 100 000. These average deviations, as will be seen, are between two and three times as large as have entered in our work.

Referring to page 338 of von Steinwehr's 1908 article we find that the maximum amount of electrolyte used was 95 cc, which corresponds almost exactly to our smallest size of voltameter. We think if he had used larger sizes of voltameter (about 350 cc), such as have been used by the N P L, L C E, and B S, that he would have found the volume effect himself. Satisfactory tests for the volume effect can not be made without using bowls differing considerably in volume. Such small bowls as used at the Reichsanstalt would not be expected to show it.

V. CONCLUSIONS AND SUMMARY

This paper concludes the experimental work which has been done at the Bureau of Standards on the silver voltameter as an international standard. Some further work on a few remaining problems including the determination of the purity of the deposited silver has been planned, but will be done elsewhere. In this, the Bureau will cooperate. The measurement of the Faraday has been carried out jointly with Dr. S. J. Bates, of the University of Illinois, who used the iodine voltameter simultaneously with the silver voltameter at this Bureau. The results of this work are to be published shortly.

Following this paper we shall publish a general summary of the work done here with the object of presenting the recent developments as concisely and completely as possible. We shall also include our draft of proposed specifications which are the natural outcome of our work, trusting that they may be of value when the international specifications are formulated for general adoption.

The principal points considered in the present paper are:

1. A determination of the voltage of the Weston normal cell using the porous cup and the Smith form voltameters. These are

found to be in substantial agreement and give the value 1.01827 volts at 20°.

2. A study of the effect of acid in the voltameter has shown a quantitative relation expressed by the equation $y = -4.5x + 0.02x^2$ to hold between the acidity of the electrolyte (x) and the resulting decrease in deposit (y) both expressed in parts per million, provided the electrolyte is pure. If the electrolyte be impure, the results can not be predicted.

3. We have studied the influence of septa other than filter paper and have found the porous pots made by the Königlich Porzellan Manufaktur when properly prepared and used to be a safe and efficient separator of anode and cathode.

4. We have made some experiments on the inclusions of the deposited silver and conclude that when pure electrolyte is employed no appreciable inclusions exist.

5. We have found the conditions under which the silver voltameter may be said to be reversible so that the current may be measured by the loss of the anode as well as the gain of the cathode. This is scientifically interesting since it adds to the evidence already obtained to disprove the heavy anode ion theory, but is of little practical importance.

Finally, we believe that the silver voltameter has shown itself to be an instrument of precision and capable of checking the constancy of the Weston normal cell according to the decision of the London conference.

WASHINGTON, December 1, 1913.



